

Chemical Sensor and Actuators

The tongue and the nose

Two of our most important chemical sensors, the tongue and the nose not only share a close and connected space but also cooperate in determining taste. The tongue is a multifunction muscle, perhaps the most flexible in the body. Taste, the chemical analysis of substances that come in contact with the tongue, is processed by taste buds or sensors and can detect five distinct flavors: salty, sour, bitter, sweet, and savory. Although taste buds are found mostly on the tongue, some can be found as well on the soft palate, upper esophagus, and epiglottis (the area in the back of the mouth between the tongue and the larynx). Most taste buds reside in protrusions on the surface of the tongue and open toward its upper surface, an opening through which food elements come in contact with it (gustatory pore). The human tongue may contain upwards of 8000 taste buds or as few as 2000, depending on individual variations and on age. Taste is transmitted through nerves to the gustatory section of the brain.

The tongue has other functions as well. In humans it is an integral part of processing food and cleaning the mouth and, significantly, of speech. As such it serves as a mechanical organ. In some animals it is part of the heat regulation mechanism (as, e.g., in dogs). In many animals it serves as an indispensable hygienic function in cleaning fur or drinking (e.g., in cats) and the cleaning of soft organs (such as cleaning the eyes in some reptiles or the muzzle in bovines). Specialized functions of the tongue can be found, an example being the prehensile tongue of the chameleon or the elongated tongue of the giraffe serving as a hook for feeding purposes.

The second chemical organ is the nose. It consists of a relatively simple structure with its external, visible protrusion and its two nostrils. Internally it has a number of functions. Immediately behind the nostrils are three bony surfaces called conchae that force and regulate the air flow downward toward the lungs. These also warm the air and, together with a mucous surface and hairs, filter the air of debris and dust. Soft tissue on their sides also controls the amount of air and its speed by constricting or enlarging the opening. Above, in the upper part of the nose cavity and out of the main airstream, a separate cavity contains the olfactory organ, the cells that are responsible for smell. This cavity is open toward the airstream, sampling the air, but because air does not flow through it, the molecules linger in it long enough to accomplish the smelling function. It is for this reason that smells sometimes seem to linger long after their causes have disappeared. The olfactory cells are connected to the olfactory section of the brain. The sense of smell is usually not considered as critical as that of sight or hearing, but it is somehow connected with long-term memory. Long after the sights or sounds of an event have faded, the odors of a place or a situation linger in the brain, still vivid and evoking. The nose also has certain adaptations. In most mammals the nose has a secondary olfactory bulb called the vomeronasal organs that sense certain chemical messages associated with social and sexual conditions. These organs bypass the cerebral cortex and link to sections in the brain responsible for reproduction and maternity and also affect aggressiveness in males. Another adaptation in some reptiles (snakes, lizards) is the combination of a forked tongue that samples the air and deposits molecules into an organ (called the Jacobson organ) on the roof of the mouth to chemically sense the environment.

8.1 | INTRODUCTION

To most, chemical sensors are likely to be the least understood of sensors and least known, even though they are common in the home, transportation, and places of work. The principles involved are often very different than those applied to other sensors and the method of sensing may be different as well. In many chemical sensors, sampling of a substance occurs. The sample is then allowed to interact in some fashion with elements of the sensor and usually an electric output is obtained from this reaction. Some sensors perform a complete analysis of the substance, while in others a direct output is obtained simply from the presence of the substance. Even the units involved are sometimes obscure to all but those versed in chemistry or chemical engineering.

However, chemical sensing is no different than other areas of sensing in that stimuli are involved, a physical sensor is employed, and the output is used to affect an appropriate action. It is worth reiterating that chemical sensors are very common and the role of chemical sensing is only likely to increase as the need for more stringent environmental monitoring and protection increases. An important role of sensors is in environmental monitoring, protection and tracking of hazardous materials, as well as the use of chemical sensors to track natural and man-made occurrences, including pollution, waterways infestation, migration of species, and, of course, weather prediction and tracking. In the sciences and in medicine, the sampling of substances such as oxygen, blood, and alcohol is well known. The food industry relies on them heavily in monitoring food processing and food safety and the military has been using chemical sensors at least since World War I to track chemical agents used in chemical warfare. Pollution control in vehicles is done on a vast scale with literally billions of chemical sensors in use. And just as important are the uses around the home: carbon monoxide (CO) detectors, smoke alarms, pH meters, and many more.

And chemical actuators also exist. We tend to think of actuators in terms of mechanical actuation, although by now it should be clear that any action taken by a system may be viewed as an output of that system and hence qualifies as actuation. In that sense, chemical actuators are those devices and processes that perform a chemical reaction or process to affect a specific outcome. For example, chemical scrubbers, whose role is to remove a substance or substances (usually for purposes of pollution control), are an important class of chemical actuators. Also used for pollution control is the catalytic converter, whose best-known use is in vehicles. And if mechanical actuation is easier to conceptualize, then the internal combustion engine or the deployment of an airbag during an accident may be good examples of actuators that may be termed chemical (although they may equally well be called mechanical actuators).

The plethora of applications and devices presents another problem—how to classify chemical sensors and actuators and the proper approach for their presentation. It seems that the first level of distinction between chemical stimuli is between a direct and indirect output. In a direct sensor, the chemical reaction or the presence of a chemical produces a measured electrical output. A simple example is the capacitive moisture sensor—the capacitance is directly proportional to the amount of water (or other fluid) present between its plates. An indirect (also called complex) sensor relies on a secondary, indirect reading of the sensed stimulus. For example, in an optical smoke detector, an optical sensor such as a photoresistor is illuminated by a source and

establishes a background reading. Smoke is “sampled” by allowing it to flow between the source and sensor and alter the light intensity, its velocity, its phase, or some other measurable property. Some chemical sensors are much more complex than that and may involve more transduction steps. In fact, some may be viewed as complete instruments or processes.

Another distinction that can be made is on the basis of the stimulus itself. For example, the sensing of stimuli such as acidity, conductivity, and oxidation–reduction potential may form the basis of a classification.

We will avoid a rigid classification and will concentrate on those chemical sensors that are most important from a practical point of view while trying to cover the principles involved in chemical sensing. In doing so, we will try to steer clear of most chemical reactions and the formulas associated with them, replacing these with physical explanations that convey the process and explain the results without the baggage of analytic chemistry. We will start with the class of electrochemical sensors. This class includes those sensors that convert a chemical quantity directly into an electrical reading and follows the definition above for direct sensors. The second group is those sensors that generate heat and where heat is the sensed quantity. These sensors, just like the thermo-optical sensors in **Chapter 4**, are indirect sensors, as are the optical chemical sensors. Following these are some of the most common sensors, such as pH and gas sensors. Humidity and moisture sensors are included here even though their sensing is not truly chemical, but because the sensing methods and materials relate to chemical sensors.

8.2 | CHEMICAL UNITS

Most units used in conjunction with chemical sensors and actuators are the same as in other disciplines, but there are a few that are unique. These are defined here before we use them.

Mole (mol): the only chemical base SI unit, defined as an amount of substance equal to approximately 6.02214×10^{23} (Avogadro’s number) molecules of that substance. Units of millimole (mmol), kilomole (kmol), etc., are sometimes employed.

Molar mass (g/mol): the mass in grams of a mole of a substance.

Gram-equivalent (g-eq): the mass of 1 equivalent, that is, the mass of a given substance that will either (1) supply or react with 1 mole of hydrogen cations (H^+) in an acid/base solution or (2) supply or react with 1 mole of electrons in an oxidation–reduction (redox) reaction. The gram-equivalent is more general than that and for general purpose use is equal to the molar mass (mass/mole) divided by the valence of the atom or molecule being considered.

Parts per million (ppm) and parts per billion (ppb): dimensionless quantities that in their most common usage represent a fraction of a quantity, such as a mass fraction ($1 \text{ mg/kg} = 1 \text{ ppm}$ or $10 \text{ } \mu\text{g/kg} = 10 \text{ ppb}$). However, it can represent any other fraction. These notations are used in the same fashion as the percent (%) to indicate the fraction of one species into the whole. Although not strictly correct, it is sometimes used to represent a change with respect to a variable.

For example, we may say that the change is 1 ppm/°C. Or we may say that the change in volume of a material is 100 ppm/°C, meaning that the change in volume is $100 \mu\text{m}^3/\text{m}^3/^\circ\text{C}$. The units ppm and ppb are not part of the SI system, but are universally accepted and commonly used in chemistry and medicine. Any use of ppb should be undertaken carefully, as the billion has two different meanings. In the United States the billion is used as the so-called short scale: 1 billion = 10^9 . The traditional value for billion is the long scale: 1 billion = 10^{12} . The unit ppm refers to the short scale (1 ppm = one part in 10^6).

EXAMPLE 8.1**Conversion between mole and mass**

The mole is not a fixed quantity, that is, a mole of one substance represents a different mass than a mole of another substance. Consider oxygen, hydrogen, and water. A mole of each has the same number of molecules or atoms, but the masses are different. To convert from moles to mass (or vice versa) we use the atomic units of the substance.

Oxygen has an atomic mass equal to 16 amu (atomic mass units). Therefore 1 mole represents a mass of 16 g. Hydrogen has an atomic mass equal to 1.008 amu. Thus 1 mole of hydrogen has a mass of 1.008 g. Water (H_2O) has atomic mass of $2 \times 1.008 + 16 = 18.016$ amu. The mass of 1 mole of water is 18.016 g. The molar mass is calculated from the atomic mass of the constituents of the substance by adding the masses of all constituents in 1 mole.

8.3 | ELECTROCHEMICAL SENSORS

An electrochemical sensor is expected to exhibit changes in resistance (conductivity) or changes in capacitance (permittivity) due to substances or reactions. These may carry different names. For example, potentiometric sensors are those that do not involve current, only measurement of capacitance and voltage. Amperimetric sensors rely on measuring current, whereas conductimetric sensors rely on measurement of conductivity (resistance). These are different names for the same properties since voltage, current, and resistance are related by Ohm's law.

Electrochemical sensors include a large number of sensing methods, all based on the broad area of electrochemistry. Many common devices, including fuel cells (an actuator), surface conductivity sensors, enzyme electrodes, oxidation sensors, and humidity sensors, belong to this category. We shall start with some of the simplest and most useful sensors available, the metal oxide sensors.

8.3.1 Metal Oxide Sensors

Metal oxide sensors rely on a very well-known property of metal oxides at elevated temperatures to change their surface potential, and therefore their conductivity, in the presence of various reducible gases such as ethyl alcohol, methane, and many others, sometimes selectively, sometimes not. Metal oxides that can be used are oxides of tin (SnO_2), zinc (ZnO), iron (Fe_2O_3), zirconium (ZrO_2), titanium (TiO_2), and wolfram (WO_3). These are semiconductor materials and may be either *p*- or *n*-type, with preference toward *n*-type materials. The fabrication is relatively simple and may be based on silicon processes or other thin or thick film technologies. The basic principle is that

when an oxide is held at elevated temperatures, the surrounding gases react with the oxygen in the oxide, causing changes in the resistivity of the material. The essential components are the high temperature, the oxide, and the reaction in the oxide.

As a representative sensor, consider the carbon monoxide (CO) sensor shown in **Figure 8.1a**. It consists of a heater and a thin layer of tin dioxide (SnO_2) above it. In terms of construction, a silicon layer is first created to serve as a temporary support for the structure. Above it, a silicon dioxide (SiO_2) layer is thermally grown. This layer must be capable of withstanding high temperatures. A layer of gold is sputtered on top of the SiO_2 layer and etched to form a long meandering wire that serves as the heating element by driving it with a sufficiently high current. A second layer of SiO_2 is deposited on top, sandwiching the gold heating element. Then the SnO_2 layer is sputtered on top and patterned with grooves to increase its active surface. The original silicon material is finally etched away to decrease the heat capacity of the sensor. The sensing area can be quite small: 1–1.5 mm². The device is heated to 300°C to operate, but because the size is very small and the heat capacity is small as well, the power needed is typically small—on the order of 100 mW. The conductivity of the oxide can be written as

$$\sigma = \sigma_0 + kP^m \quad [\text{S/m}], \quad (8.1)$$

where σ_0 is the conductivity of the SnO_2 at 300°C but without CO present, P is the concentration of the CO gas [ppm], k is a sensitivity coefficient (determined experimentally for various oxides), and the exponent m is again an experimental value, which for SnO_2 is about 0.5. Thus the conductivity increases with an increase in concentration, as shown in **Figure 8.1b**. The resistance is proportional to the inverse of conductivity, so it may be written as

$$R = aP^{-\alpha} \quad [\Omega], \quad (8.2)$$

where a is a constant defined by the material and construction, α is an experimental quantity for the gas, and P is its concentration [ppm]. This simple relation defines the response of the sensor to various gases, but only on a range of concentrations since it cannot define the resistance at zero concentration. The response is exponential (linear on a log scale) and a transfer function of the type shown in **Figure 8.1b** must be defined for each gas and each type of oxide. SiO_2 -based sensors as well as ZnO sensors can also be used to sense carbon dioxide (CO_2), toluene, benzene, ether, ethyl alcohol, and propane with excellent sensitivity (1–50 ppm).

A variation of the structure above is shown in **Figure 8.2**. It consists of an SnO_2 layer on a ferrite substrate. The heater here is provided by a thick layer of rubidium dioxide (RuO_2) fed through two gold contacts (C and D). The resistance of the very thin SnO_2 layer (less than about 0.5 μm) is measured between the two gold contacts on top (A and B). This sensor, which operates as above, is sensitive primarily to ethanol and CO.

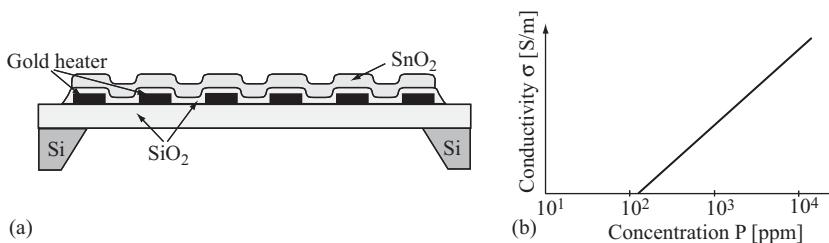
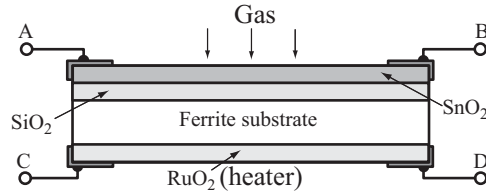


FIGURE 8.1 ■
A metal oxide CO sensor.
(a) Construction.
(b) Transfer function.

FIGURE 8.2 ■
An ethanol and CO
sensor.



EXAMPLE 8.2 Alcohol sensor

An alcohol sensor is made by deposition of a thin layer of tungsten trioxide (WO_3) nanoparticles on a substrate. To evaluate its performance, the resistance of the sensor is measured at two concentrations. At 100 ppm the resistance is 161 k Ω , while at 1000 ppm its resistance is 112 k Ω . The resistance of the sensor in air in the absence of alcohol is 320 k Ω . Calculate the sensitivity of the sensor in ohms/ppm.

Solution: We can use **Equation (8.2)** to evaluate the constants a and α . Then we can calculate the sensitivity based on the definition.

At 100 ppm,

$$R_1 = 161,000 = a100^{-\alpha} \quad [\Omega].$$

At 1000 ppm,

$$R_2 = 112,000 = a1000^{-\alpha} \quad [\Omega].$$

To evaluate the constants we take the natural logarithm on both sides of both relations:

$$\ln 161,000 = \ln a - \alpha \ln(100)$$

$$\ln 112,000 = \ln a - \alpha \ln(1000).$$

Subtracting the second relation from the first we get

$$\ln 161,000 - \ln 112,000 = \alpha \ln(1000) - \alpha \ln(100),$$

or

$$\alpha = \frac{\ln 161,000 - \ln 112,000}{\ln 1000 - \ln 100} = \frac{\ln\left(\frac{161}{112}\right)}{\ln 10} = 0.1576.$$

Substituting back into either relation we get

$$\ln a = \ln 112,000 + \alpha \ln(1000) = \ln 112,000 + 0.1576 \ln(1000) = 12.7149.$$

Therefore

$$a = e^{12.7149} = 332,667.$$

The relation for resistance now becomes

$$R = 332,667P^{-0.1576} \quad [\Omega]$$

The sensitivity may be written as

$$S = \frac{dR}{dP} = -0.1576 \times 332,667P^{-1.1576} = -52,428P^{-1.1576} \quad [\Omega/\text{ppm}].$$

The sensitivity varies along the curve as expected. For example, at 500 ppm the sensitivity is 39.37 Ω/ppm , whereas at 200 ppm it is 113.73 Ω/ppm .

As mentioned above, the reaction is with oxygen, and hence any reducible gas (a gas that reacts with oxygen) will be detected. This lack of selectivity is a common problem in metal oxide sensors. To overcome this problem, one can select temperatures at which the required gas reacts but not others or the particular gas may be filtered. These sensors are used in many applications, from CO and CO₂ detectors to oxygen sensors in automobiles. The latter, for example, uses a TiO₂ sensor built as above in which resistance increases in proportion to the concentration of oxygen. This is commonly used in other applications, such as the sensing of oxygen in water (for pollution control purposes). The process can also be used to determine the amount of available organic material in water by first evaporating the water and then oxygenating the residue to determine how much oxygen is consumed. The amount of oxygen consumed in the reaction is then an indication of the amount of organic material in the sample.

8.3.2 Solid Electrolyte Sensors

Another important type of sensor that has found significant commercial applications is the solid electrolyte sensor, most often used in oxygen sensors, including those in automobiles. In these sensors a solid galvanic cell (battery cell) is built that produces an emf across two electrodes based on the oxygen concentrations at the two electrodes under constant temperature and pressure. A solid electrolyte, usually made of zirconium dioxide (ZrO₂) and calcium oxide (CaO) in a roughly 90%:10% ratio, is often used because it has high oxygen ion conductivity at elevated temperatures (above 500°C). The electrode is made of sintered ZrO₂ powder (sintering makes the powder into a ceramic). The inner and outer electrodes are made of platinum that act as catalysts and absorb oxygen. The structure is shown in **Figure 8.3** for an exhaust oxygen sensor in an automobile. The potential across the electrodes is

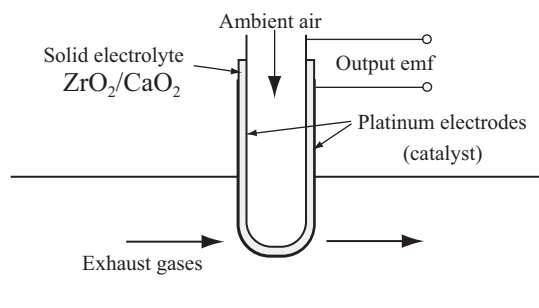


FIGURE 8.3 ■ A solid electrolyte oxygen sensor for car engines used as an active sensor.

$$emf = \frac{RT}{4F} \ln \left(\frac{P_{O_2}^1}{P_{O_2}^2} \right) \quad [V], \quad (8.3)$$

where R is the universal gas constant (8.314472 J/K/mol), T is the temperature (K), and F is the Faraday constant (96,487 C/mol). $P_{O_2}^1$ is the concentration of oxygen in the atmosphere, $P_{O_2}^2$ is the concentration of oxygen in the exhaust, both heated to the same temperature. There is also a small constant added to the relation in **Equation (8.3)** that represents the emf when both concentrations are the same. Ideally this constant should be zero, but in practice it is not. We will leave it out, however, because it is small and because it depends on the sensor (construction, materials, etc.) and hence is taken care of in the calibration of the sensor. The oxygen sensor is used to adjust the fuel ratio at the most efficient rate at which pollutants NO and NO₂, known together as NO_x and CO are converted into N₂, CO₂, and H₂O, all of which are natural constituents in the atmosphere and hence considered nonpollutants. In a heated oxygen sensor, the oxygen concentrations in the exhaust stream produce emfs between about 2 mV for atmospheric concentration (20.6%) and about 60 mV for oxygen concentrations around 1%.

EXAMPLE 8.3**Strategies for emission control in internal combustion engines**

There are a number of strategies that can be followed to reduce emissions of noxious gases from vehicles equipped with internal combustion engines. All involve a catalytic converter and oxygen sensors (see **Section 8.9.1** for the operation of the catalytic converter) and convert CO as well as NO to benign forms such as CO₂, N₂, and H₂O₂. These are as follows:

1. The oxygen level is sensed before gasses get into the catalytic converter. This strategy is based on the premise that given enough oxygen in the exhaust stream most (if not all) gases will be converted to benign forms. This method has the advantage of simplicity—it senses relatively large concentrations of oxygen. Based on known fuel needs, the oxygen level can be increased or decreased to attain minimum emissions. However, one never knows if the oxygen is actually being used to oxidize pollutants or if it is simply released with the exhaust. A perfectly functioning or totally nonfunctioning catalytic converter would be treated the same by the control system.
2. It is possible to measure only the oxygen in the exhaust after the catalytic converter, assuming that if there is some oxygen in the exhaust stream, the catalytic converter converted all the noxious gases that could have been converted. The advantage of this method is that it indicates how much oxygen has not been consumed and can increase the oxygen levels in the intake to keep a minimum level of oxygen in the exhaust. Similarly, if too much oxygen is present it can reduce the oxygen levels, since an engine that runs too lean also runs too hot. The problem with this method is that an inefficient or nonfunctioning catalytic converter would leave too much oxygen in the exhaust, forcing the control system to reduce oxygen at the intake and forcing the engine to run too rich, increasing emissions.
3. By placing an oxygen sensor before and one after the catalytic converter, a true closed-loop control may be accomplished. In addition to controlling emissions, comparison of the readings of the two sensors can also be used for diagnostics to indicate the condition of the catalytic converter (or the absence of a converter, something that is illegal) and the sensors

themselves. Cars equipped with an onboard diagnostics (OBDII) system have two sensors and the system issues diagnostics codes covering the status of the sensors and of the catalytic converter (see **Example 1.1** for some of the sensors covered by the OBDII system). This method is optimal in the sense that it avoids the main problems associated with single-sensor systems.

A common strategy for pollution control in an internal combustion engine is to sense the oxygen concentration before and after the catalytic converter and use the readings of the oxygen sensors to adjust the fuel:air ratio in the engine to ensure full burning of noxious gases such as CO. By measuring both the input and output oxygen concentration one gets an indication of the effectiveness of the catalytic converter itself (see **Example 8.4**).

In engines that operate in a much leaner mode, the solid electrolyte sensor is not sufficiently sensitive, since in these high-efficiency engines the amount of oxygen in the exhaust is high and the reading of the electrolytic cell is insufficient. In such engines, the same basic sensor is used, that is, a solid electrolyte between two platinum electrodes, as shown in **Figure 8.4**, but a potential is applied to the cell. This arrangement forces (pumps) oxygen across the electrolyte and a current is produced proportional to the oxygen concentration in the exhaust. This sensor is called a diffusion oxygen sensor or a diffusion-controlled limiting current oxygen sensor.

Another important application of solid electrolyte sensors is in oxygen sensing in the production of steel and other molten materials, since the quality of the final product is a direct result of the amount of oxygen in the process. The sensor is shown in **Figure 8.5**. The molybdenum needle is used to keep the device from melting when it is inserted in the molten steel. A potential difference is developed across the cell (between the molybdenum and the outer layer). The voltage is measured between the inner electrode and the outer layer through an iron electrode dipped into the molten steel. The voltage developed is directly proportional to the oxygen concentration in the molten steel.

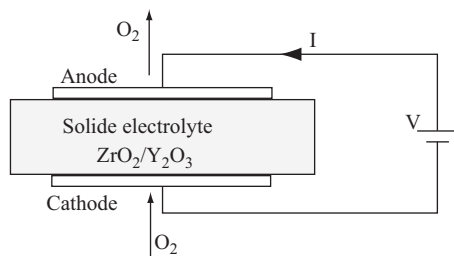


FIGURE 8.4 ■
A diffusion-controlled limiting current oxygen sensor used as a passive sensor.

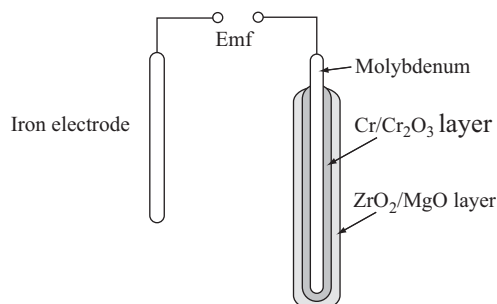


FIGURE 8.5 ■
Oxygen sensor for molten metals.

EXAMPLE 8.4**Oxygen sensors in cars: efficiency of catalytic converters**

To monitor the efficiency of a catalytic converter, one can use an oxygen sensor before and another after the catalytic converter. Taking the difference between the potentials of the two sensors makes a differential sensor and gives an indication of the conversion efficiency of the converter. The larger the difference, the more oxygen is used in the converter, and hence the higher its conversion efficiency. Suppose the oxygen content entering the converter is 10% and the minimum oxygen concentration required in the exhaust is 1%. Calculate the transfer function of the differential sensor assuming both sensors are at a temperature of 750°C.

Solution: The output of each sensor is calculated using **Equation (8.3)**. We denote P_0 , the oxygen concentration in air; P_{in} , the concentration in the exhaust before entering the converter; and P_{out} , the concentration after the converter. The potentials of the two sensors are

For the sensor in front of the converter:

$$emf_1 = \frac{RT}{4F} \ln \left(\frac{P_0}{P_{in}} \right) \quad [\text{V}].$$

The emf in the exit sensor:

$$emf_2 = \frac{RT}{4F} \ln \left(\frac{P_0}{P_{out}} \right) \quad [\text{V}].$$

Since emf_2 is necessarily larger than emf_1 , we calculate the difference as

$$emf_2 - emf_1 = \frac{RT}{4F} \ln \left(\frac{P_0}{P_{out}} \right) - \frac{RT}{4F} \ln \left(\frac{P_0}{P_{in}} \right) = \frac{RT}{4F} \ln \left(\frac{P_{in}}{P_{out}} \right) \quad [\text{V}].$$

For the given input and exhaust concentrations we get

$$\begin{aligned} \Delta emf &= emf_2 - emf_1 = \frac{RT}{4F} \ln \left(\frac{P_{in}}{P_{out}} \right) = \frac{8.314472 \times 1023.15}{4 \times 96487} (\ln P_{in} - \ln P_{out}) \\ &= 0.02204 (\ln 0.1 - \ln P_{out}) = -0.02204 \ln P_{out} - 0.05075 \quad [\text{V}]. \end{aligned}$$

That is,

$$\Delta emf = -0.02204 \ln P_{out} - 0.05075 \quad [\text{V}].$$

This transfer function is shown in **Figure 8.6** for concentrations between 0.1 (10%) and 0.01 (1%). The potential at 1% oxygen in the exhaust (after the converter) is approximately 50 mV.

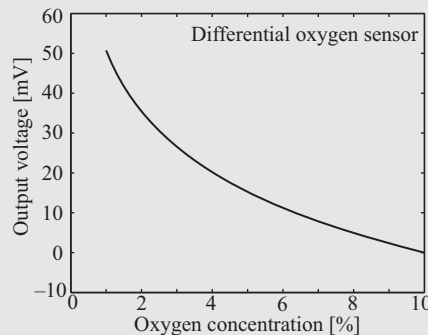


FIGURE 8.6 ■ Transfer function of a differential oxygen sensor.

This decreases with an increase in concentration until at 10% oxygen it is zero (both sensors are at the same potential since the oxygen concentrations are the same). The higher the output, the higher the efficiency of the converter (i.e., the lower the oxygen concentration in the exhaust).

8.3.3 The Metal Oxide Semiconductor (MOS) Chemical Sensor

A unique development in sensors is the use of the basic metal oxide semiconductor field-effect transistor (MOSFET) structure, commonly used in electronics, as a chemical sensor. The basic idea is that of the classic MOSFET transistor, in that the gate serves as the sensing surface. The advantage of this is that a very simple and sensitive device is obtained that controls the current through the MOSFET. The interfacing of such a device is simple and there are fewer problems (such as heating, temperature sensing, and compensation, etc.) to overcome. It is therefore not surprising that the basic MOS structure has been developed into an array of sensors for diverse applications.

For example, by simply replacing the metal gate in **Figure 8.7** with palladium, the MOSFET becomes a hydrogen sensor, since the palladium gate absorbs hydrogen and its potential changes accordingly. Sensitivity is down to about 1 ppm. Other similar structures can sense gases such as H_2S and NH_3 . Palladium MOSFETs (Pd-gate MOSFETs) can also be used to sense oxygen in water, relying on the fact that the absorption efficiency of oxygen decreases in proportion to the amount of oxygen present.

We shall say more about MOSFET sensors in the subsequent section on pH sensing, since MOSFETs have been very successful in sensing pH.

8.4 | POTENTIOMETRIC SENSORS

A large subset of electrochemical sensors is the so-called potentiometric sensors. These are based on an electric potential that develops at the surface of a solid material when immersed in a solution containing ions that can be exchanged at the surface. The potential is proportional to the number or density of ions in the solution. A potential difference between the surface of the solid and the solution occurs because of charge separation at the surface. This contact potential, analogous to that used to set up a voltaic cell, cannot be measured directly. However, if a second, reference electrode is provided, an electrochemical cell is set up and the potential across the two electrodes is directly measurable. To ensure that the potential is measured accurately, and therefore that the ion concentration is properly represented by the potential, it is critical that the current

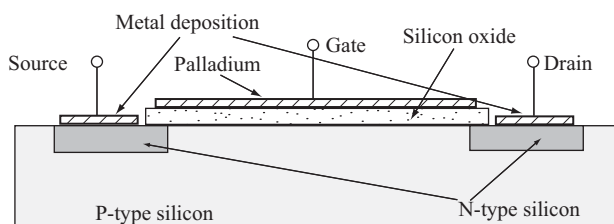


FIGURE 8.7 ■ The MOSFET structure used as a chemical sensor by replacing the gate with a species-sensitive material.

drawn by the measuring instrument is as small as possible (any current is a load on the cell and therefore reduces the measured potential).

For a sensor of this type to be useful, the potential generated must be ion specific—that is, the electrodes must be able to distinguish between solutions. These are called ion-specific electrodes or membranes. There are four types of membranes:

Glass membranes: selective for H^+ , Na^+ , NH_4^+ and similar ions.

Polymer-immobilized membranes: in this type of membrane, an ion-selective agent is immobilized (trapped) in a polymer matrix. A typical polymer is polyvinyl chloride (PVC).

Gel-immobilized enzyme membranes: the surface reaction is between an ion-specific enzyme, which in turn is either bonded onto a solid surface or immobilized into a matrix, and the solution.

Soluble inorganic salt membranes: either crystalline or powdered salts pressed into a solid are used. Typical salts are LaF_3 or mixtures of salts such as silver sulfide (Ag_2S) and silver chloride (AgCl). These electrodes are selective to fluoride (F^-), sulfur (S^{2-}), chlorine (Cl^-), and similar ions.

8.4.1 Glass Membrane Sensors

By far the oldest of the ion-selective electrodes, the glass membrane has been in use for pH sensing since the mid-1930s and is as common as ever. The electrode is a glass made with the addition of Na_2O and aluminum oxide (Al_2O_3), made into a very thin tubelike membrane. This results in a high-resistance membrane, which nevertheless allows transfer of ions across it. The pH sensor measures the concentration of H^+ ions in a solution as follows:

$$\text{pH} = -\log|\text{H}^+|, \quad (8.4)$$

where the concentration of hydrogen atoms is in terms of gram-equivalent per liter (g-eq/L). A concentration of 1 g-eq/L means a pH of 0, a concentration of 10^{-1} means a pH of 1, and so on. The normal pH scale is between 0 and 14, which corresponds to concentrations of 10^0 to 10^{-14} g-eq/L. However, pH can and is defined beyond that scale. A concentration of 10 g-eq/L will produce a pH of -1 , whereas a concentration of 10^{-18} will produce a pH of 18. The higher the concentration, the more acidic the solution, and vice versa. A pH of 7 is considered neutral simply because that is the normal pH of water. In many instances, when the solutions are weak (weak acids or bases), **Equation (8.4)** is accurate and pH measures the actual ion concentration. In strong solutions the concentration of H^+ must be multiplied by an activity factor to take into account the contribution of other ions to the pH reading. The activity factor takes into account the interaction between all ions in the solution. In this case the pH is given as

$$\text{pH} = -\log|\gamma_{\text{H}}\text{H}^+|, \quad (8.5)$$

where γ_{H} is the activity factor for the specific solution.

The basic method of pH sensing is shown in **Figure 8.8a**. In principle all that is needed is to measure the ion concentration in the solution. However, that is difficult to do directly, hence pH is sensed by using two half-cells, one with a known pH, called a reference half-cell or electrode, the other a sensing half-cell or electrode. In **Figure 8.8a**

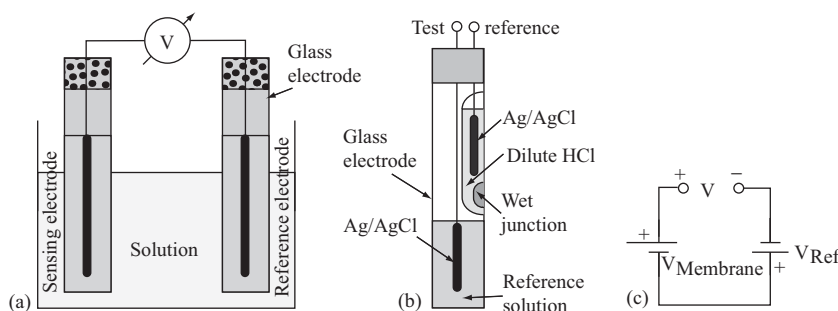


FIGURE 8.8 ■
 (a) Basic method of pH sensing using a glass membrane.
 (b) A glass membrane pH probe incorporating the reference electrode in a single unit.
 (c) Equivalent circuit.

the sensing glass membrane electrode is shown on the left and a reference electrode on the right. The reference electrode is typically a silver/silver chloride (Ag/AgCl) electrode in a potassium chloride (KCl) aqueous solution or a saturated calomel electrode (Hg/Hg₂Cl₂ in a KCl solution). The reference electrode is normally incorporated into the test electrode so that the user only has to deal with a single probe, as shown in **Figure 8.8b**. Since what is actually measured is the difference between the electrode potential and the reference potential, it is easier to understand the measurement in the equivalent circuit in **Figure 8.8c**. The potential measured by the instrument is

$$V = V_{\text{ref}} + V_{\text{membrane}} \quad [\text{V}], \quad (8.6)$$

where V_{ref} is a constant value and V_{membrane} depends on the ion concentration in the solution. The latter is given by the Nernst equation (which gives the potential of any half-cell) as

$$V_{\text{membrane}} = \frac{RT}{nF} \ln(a) = \frac{2.303RT}{nF} \log_{10}(a) = \frac{2.303RT}{nF} \text{pH} \quad [\text{V}], \quad (8.7)$$

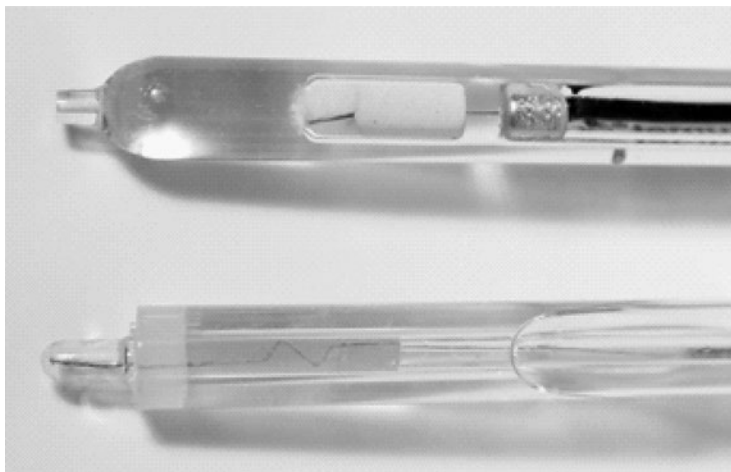
where R is the universal gas constant (equal to 8.314462 J/mol/K), F is Faraday's constant (equal to 96,485.309 C/mol), n is the net number of negative charges transferred in the reaction, a is the activity of the ions involved in the reaction, and T is the temperature of the solution [K]. The term 2.303 comes from the fact that $\ln(a) = \log_{10}(a)/\log_{10}e$, that is, $2.303 = 1/\log_{10}e$. For H^+ ions, $n = 1$ (one electron transferred) and $\log_{10}(a)$ is the pH, leading to the following relation for pH by substituting **Equation (8.7)** into **Equation (8.6)**:

$$\text{pH} = \frac{(V - V_{\text{ref}})F}{2.303RT}. \quad (8.8)$$

Note that the activity a is an effective concentration, that is, the equivalent concentration that takes into account all interactions between ions. As indicated above, in weak acids or bases a represents the actual concentration. When the activity is less than 1, it is given as a fraction (e.g., 0.9).

In a measurement, V is the actual quantity measured—the rest of the quantities are taken into account internally. For this reason it is important for the voltage to be constant and stable and that the temperature is either taken into account or is compensated in the circuit itself. The voltage of the reference electrode is typically known or can be calculated from **Equation (8.7)**. For example, the saturated calomel (Hg/Hg₂Cl₂) (see **Figures 8.8** and **8.9**) electrode mentioned above has a potential of +0.244 V.

FIGURE 8.9 ■
A saturated calomel
reference electrode
(top) and a pH
electrode (bottom).



The Ag/AgCl electrode has a potential of +0.197 V. The copper/copper sulfate (Cu/CuSO₄) electrode has a potential of +0.314 V. There are of course other reference electrodes that can be used. **Figure 8.9** shows a saturated calomel and a pH electrode.

The pH sensor is used by first immersing the electrode into a conditioning solution of hydrochloric acid (HCl) (0.1 mol/L) and then immersing it into the solution to be tested. The electric (voltage) output is calibrated directly in pH.

Modifications of the basic configuration, both in terms of the reference electrode (filling) and the constituents of the glass membrane, lead to sensitivity to other types of ions as well as to sensors capable of sensing concentrations of dissolved gas in solutions, particularly ammonia, but also CO₂, sulfur dioxide (SO₂), hydrogen fluoride (HF), hydrogen sulfide (H₂S), and hydrogen cyanide (HCN). In essence a pH-like electrode sensitive to the desired ions is used to sense the concentration of the respective ions in solutions. These sensors are important devices in industrial processes, in pollution control, and in environmental sensing.

EXAMPLE 8.5

Basic pH measurement

An uncompensated pH sensor is used to sense the pH in a fish tank.

- Calculate the voltage measured using a saturated calomel reference electrode if the water is neutral (pH = 7) and the sensor is calibrated at 20°C.
- Calculate the error in the voltage reading of the sensor if the temperature increases by 15°C. What is the expected pH reading at 35°C?

Solution:

a. We can use **Equation (8.8)** directly to calculate V since the reference voltage of the saturated calomel electrode is 0.244 V and the calibrated pH is 7. Thus we have

$$7 = \frac{(V - 0.244)F}{2.303RT} \rightarrow V = \frac{7 \times 2.303 \times 8.314462 \times 293.15}{9.64 \times 10^4} + 0.244 = 0.6516 \text{ V.}$$

b. To calculate error we write

$$\text{pH} = \frac{(V - 0.244) \times 9.64 \times 10^4}{2.303 \times 8.314462} T^{-1}.$$

The voltage read by the instrument may be written as

$$\begin{aligned} V &= \frac{7 \times 2.303 \times 8.314462 \times T}{9.64 \times 10^4} + 0.244 = 13.9043 \times 10^{-4} T + 0.244 \\ &= 13.9043 \times 10^{-4} \times 308.15 + 0.244 = 0.6725 \text{ V}. \end{aligned}$$

This is an error of $0.6725 - 0.6516 = 0.0209 \text{ V}$ or

$$e = \frac{0.6725 - 0.6516}{0.6516} \times 100\% = 3.2\%.$$

The expected pH can again be calculated from **Equation (8.8)** since we have the potentials at the given temperature:

$$\text{pH} = \frac{(V - V_{\text{ref}})F}{2.303RT} = \frac{(0.6725 - 0.244) \times 9.64 \times 10^4}{2.303 \times 8.314462 \times 308.15} = 7.00064.$$

The error is rather small because of the logarithmic nature of the pH reading.

8.4.2 Soluble Inorganic Salt Membrane Sensors

These membranes are based on soluble inorganic salts, which undergo ion exchange interaction in water and generate the required potential at the interface. Typical salts are lanthanum fluoride (LaF_3) and silver sulfide (Ag_2S). A membrane made of these materials may be either a single crystal membrane, a disk made of sintered powdered salt, or the powdered salt may be embedded into a polymer matrix, each of these leading to sensors of similar operation but different properties and sensitivities.

The structure of a sensor used to sense the fluoride concentration in water is shown in **Figure 8.10**. The sensing membrane is made in the form of a thin disk of LaF_3 grown as a single crystal. The reference electrode is created in the internal solution (in this case a sodium fluoride/sodium chloride [NaF/NaCl] solution in 0.1 mol/L solution). The sensor shown can detect concentrations of fluoride in water between 0.1 and 2000 mg/L. This sensor is commonly used to monitor fluoride in drinking water (normal concentration of about 1 mg/L).

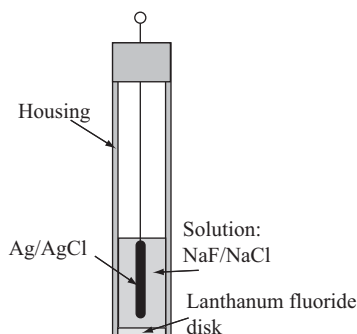


FIGURE 8.10 ■ Soluble inorganic salt membrane sensor for fluoride.

Membranes may be made of other materials, such as Ag_2S , which is easily made into thin sintered disks from powdered material and may be used in lieu of the single crystal. Also, in this form, other compounds may be added to affect the properties of the membrane, and hence its sensitivity to other ions. This leads to selective sensors sensitive to ions of chlorine, cadmium, lead, and copper, which are often used to sense for dissolved heavy metals in water.

Polymeric membranes are made by using a polymeric binder for the powdered salt in a ratio of about 50% salt and 50% binding material. The common binding materials are PVC, polyethylene, and silicon rubber. In terms of performance, these membranes are similar to sintered disks.

8.4.3 Polymer-Immobilized Ionophore Membranes

A development in the inorganic salt membrane is the use of polymer-immobilized membranes. In these, ion-selective organic reagents are used in the production of the polymer by including them in the plasticizers, particularly for PVC. A reagent, called an ionophore (or ion exchanger), is dissolved in the plasticizer at a concentration of about 1%. This produces a polymer film, which can then be used as the membrane, replacing the crystal or disk as the membrane in sensors. The construction of the sensor is simple and is shown in **Figure 8.11**. The sensor shown includes an Ag/AgCl reference electrode. The resulting sensor is a relatively high-resistance sensor. A different approach to building polymer-immobilized ionophore membranes is shown in **Figure 8.12**. It is made of an inner platinum wire on which the polymer membrane is coated and the wire is protected with a coating of paraffin. This is called a coated wire electrode. To be useful a reference membrane must be added.

FIGURE 8.11 ■ Polymer-immobilized ionophore membrane sensor.

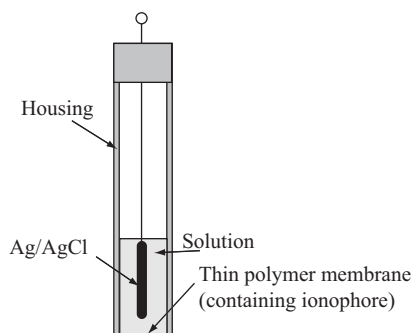
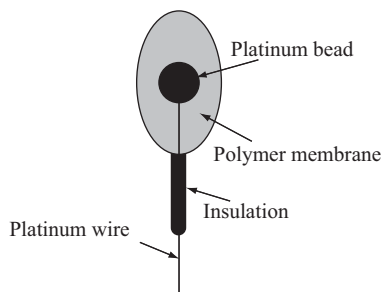


FIGURE 8.12 ■ Coated wire electrode.



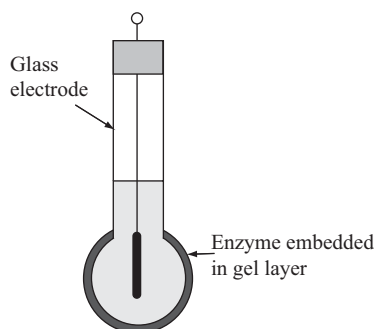


FIGURE 8.13 ■ Gel-immobilized enzyme membrane sensor.

Polymer membranes of this type can be made selective to many ions by the use of different ionophores. Sensitivity to calcium and potassium can be designed and these two types of sensors are routinely used to sense calcium in the blood and potassium in seawater. Nitrate-selective membranes are also available for sensing of nitrates in soil (fertilizers) and in runoff from fertilized fields.

8.4.4 Gel-Immobilized Enzyme Membranes

These sensors are similar in principle to polymer-immobilized ionophore membranes, but instead a gel is used and the ionophore is replaced by an enzyme designed to be selective to a particular ion. The enzyme, a biomaterial, is immobilized in a gel (polyacrylamide) and held in place on a glass membrane electrode, as shown in **Figure 8.13**. The choice of the enzyme and the choice of the glass electrode define the selectivity of the sensor. These sensors exist for the sensing of a variety of important analytes, including urea and glucose, L-amino acids, penicillin, and others. The operation is simple: The sensor is placed in the solution to be sensed, which diffuses into the gel and reacts with the enzyme. The ions released are then sensed by the glass electrode. Although these sensors are slow in response because of the need for diffusion, they are very useful in analysis in medicine, including the analysis of blood and urine.

EXAMPLE 8.6 Sensing of fluoride in water

Fluoride is an important additive to water, particularly useful for dental health in children. In addition to its use in drinking water, it is often added to toothpaste to strengthen the enamel on teeth. Sensing of the concentration of fluoride in solutions is typically done with the configuration in **Figure 8.10**. The LaF_3 disk serves as the sensing membrane sensitive to F^- ions, whereas the reference is the Ag/AgCl electrode with a potential of 0.199 V. To test for concentrations of fluoride one assumes the concentration is very low, otherwise the test shows activity rather than actual concentration. In many cases the concentration is given in ppm or ppb. The potential of the electrode can be calculated using **Equation (8.7)**, but since fluoride is a negative ion, $n = -1$. We will calculate it at 25°C :

$$\begin{aligned}
 V_{\text{membrane}} &= \frac{2.303RT}{nF} \log_{10}(a) = -\frac{2.303 \times 8.314462 \times 298.15}{1 \times 9.64 \times 10^4} \log_{10}(a) \\
 &= 0.05922 \log_{10}(a) \quad [\text{V}].
 \end{aligned}$$

As mentioned above, a represents the concentration when it is small and the membrane voltage represents the half-cell voltage (across the LaF_3 crystal). The voltage measured is given in Equation (8.6):

$$V = V_{\text{ref}} + V_{\text{membrane}} = 0.199 - 0.05922 \log_{10}(a) \quad [\text{V}].$$

This relation allows immediate calculation of the concentration from the measured voltage, V :

$$\log_{10}(a) = -\frac{V - 0.199}{0.05922}.$$

If this voltage were to be measured with a pH meter, the pH reading would then represent the concentration of a .

For example, a reading of 0.35 V represents a concentration of

$$\log_{10}(a) = -\frac{0.35 - 0.199}{0.05922} = -\frac{0.151}{0.05922} = -2.5498 \rightarrow a = 0.002819.$$

Note that the higher the concentration, the lower the measured voltage.

Of course, an instrument used to sense fluoride would typically be calibrated in ppm or in any other convenient representation such as percentage.

8.4.5 The Ion-Sensitive Field-Effect Transistor (ISFET)

Also called the chemFET, this is essentially a MOSFET in which the gate has been replaced by an ion-selective membrane. Any of the membranes discussed above may be used, but the glass and polymeric membranes are most common. In its simplest form, a separate reference electrode is used, but a miniaturized reference electrode may be easily incorporated within the gate structure as shown in **Figure 8.14a**. The gate is then allowed to come in contact with the sample to be tested and the drain current is measured to indicate the ion concentration. The most important use of this device is for measurements of pH, in which capacity the chemFET replaces the glass membrane. Other applications are in the sensing of ions such as calcium (Ca^{++}), manganese (Mn^{++}), and potassium (K^+) through the use of immobilized ionophore membranes. ChemFET pH sensors are sold commercially and in many applications are considered more appropriate than glass pH sensors, if for no other reason than they are sturdier. However, they are relatively expensive.

Figure 8.14a shows the basic structure of the ISFET. The electronic circuit in **Figure 8.14b** and the equivalent circuit in **Figure 8.14c** explain the operation. The

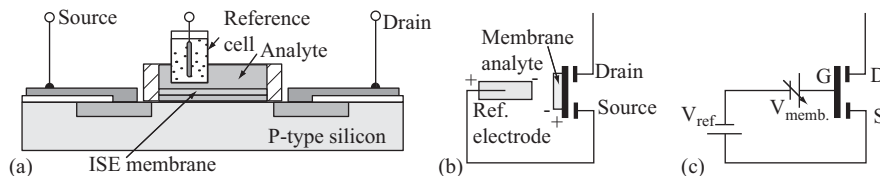


FIGURE 8.14 ■ (a) Structure of the ISFET. Note the reference electrode built into the sensor. (b) The reference and sensing membranes. (c) Equivalent circuit.

reference electrode produces a potential based on **Equation (8.7)**. This is a fixed potential that depends on the reference electrode, which is typically a saturated calomel electrode. The membrane also develops a potential based on **Equation (8.7)**, but that potential varies based on either the pH of the solution or the ion concentration in the solution. The variable voltage provided by the membrane defines the current in the MOSFET, and hence the output of the sensor. The typical sensitivity at the gate is 30–60 mV per pH unit or per concentration unit of ions (i.e., $\log_{10}a$).

8.5 | THERMOCHEMICAL SENSORS

Thermochemical or calorimetric sensors form a class of sensors that rely on the heat generated in chemical reactions to sense the amount of particular substances (reactants) involved. There are three basic sensing strategies, each leading to sensors for different applications. The most obvious is to sense the temperature increase due to a reaction using a temperature sensor such as a thermistor or thermocouple. The second type is a catalytic sensor used for sensing of flammable gases. The third measures the thermal conductivity in air due to the presence of the sensed gas.

8.5.1 Thermistor-Based Chemical Sensors

The basic principle is to sense the small change in temperature due to the chemical reaction. Since the increase in temperature is due to the reaction, a reference temperature sensor is usually employed to sense the temperature of the solution, then the difference in temperature is related to the concentration of the sensed substance. The most common approach is to use an enzyme-based reaction because enzymes are highly selective (so that the reaction can be ascertained) and because they generate significant amounts of heat. A typical sensor is made by coating the enzyme directly on the thermistor. The thermistor itself is a small bead thermistor, making for a very compact, highly sensitive sensor. The construction is shown in **Figure 8.15**. This sensor has been used to sense the concentration of urea and glucose, each with its own enzyme (urease or glucose enzymes, respectively). The amount of heat generated is proportional to the amount of the substance sensed in the solution. The temperature difference between the treated thermistor and the reference thermistor is then related to the concentration of the substance. In general, the heat lost or gained depends on the change in enthalpy in the reaction. Only part of that energy contributes to the change in temperature of the

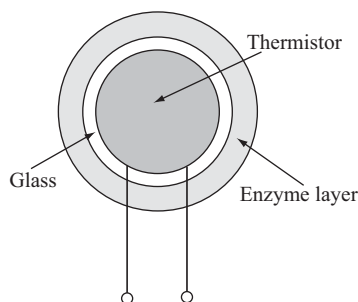


FIGURE 8.15 ■ A thermochemical sensor as used to sense urea or glucose (depending on the enzyme used), making use of a small bead thermistor.

sensor, depending on the environment and the heat capacity of that environment. In air and other gases the specific heat capacity is rather high and most if not all of the heat generated contributes to the temperature change in the sensors. In solutions, particularly aqueous solutions, some of the heat is absorbed by the solution and does not contribute to the change in temperature. This also depends on the speed of the reaction. Fast reactions tend to be more accurate, as less heat is conducted away from the sensors. The heat produced by the reaction increases the temperature of the sensor through the self-heat relation of the thermistor. Given a change in enthalpy ΔH [J], the change in temperature of the sensor (the thermistor, enzyme layer, and the immediate vicinity) with specific heat capacity C_p is

$$\Delta T = \frac{\Delta H}{C_p} n \quad [^{\circ}\text{C}], \quad (8.9)$$

where ΔH is typically given in J/mol, C_p in J/mol/K, and n is the number of moles of analyte taking part in the reaction (dimensionless). In some cases ΔH is available in J/g or kJ/kg. In these cases C_p must also be in J/g/K or in kJ/kg/K. It should be remembered also that one can convert from mass to moles and vice versa through use of the atomic masses of the substances involved. Clearly each substance involved, including the sensor, the enzyme, and the solution (or air), will have its own heat capacity, but it is likely that the heat capacity of the sensor will dominate (i.e., it is typically lower than the surroundings), or some average heat capacity can be used, perhaps from a calibrated test. Given the change in temperature, $\Delta T = T - T_0$, the change in resistance of a thermistor is given by **Equation (3.12)**:

$$R(T) = R(T_0)e^{\beta(1/T - 1/T_0)} \quad [\Omega], \quad (8.10)$$

where the resistance now changes from $R(T_0)$ to $R(T) = R(T_0 + \Delta T)$. These relations are useful provided the change in enthalpy can be captured and the heat capacity is known. Otherwise the response of the temperature sensor (in this case a thermistor) must be established experimentally for every reaction and environment (solution). The temperature T can be measured with a sensor identical to that in **Figure 8.15**, but without the enzyme layer, and hence not taking part in the reaction.

Although some thermistors can measure temperature differences as low as 0.001°C , most are less sensitive than that, and the overall sensitivity of the sensor depends on the amount of heat generated. In the examples above, the glucose reaction is much more sensitive than the urea reaction because glucose has a much higher enthalpy.

8.5.2 Catalytic Sensors

These are true calorimetric sensors in the sense that a sample of the analyte is burned and the heat generated in the process is measured through a temperature sensor. This type of sensor is common and serves as the main tool in the detection of flammable gases such as methane, butane, carbon monoxide, and hydrogen, fuel vapors such as gasoline, as well as flammable solvents (ether, acetone, etc.). The basic principle is the sampling of air containing the flammable gas into a heated environment that combusts the gas and generates heat. A catalyst is used to speed up the process. The temperature sensed is then indicated as a percentage of flammable gas in air.

The simplest form of the sensor is to use a current-carrying platinum coil. The platinum coil has two purposes. It heats up due to its own resistance and it serves as a catalyst for hydrocarbons (this is the reason why it is the active material in catalytic converters in automobiles). Other, better catalysts are palladium and rhodium, but the principle is the same. The gas combusts and releases heat, raising the temperature, and hence the resistance, of the platinum coil. This change in resistance is then a direct indication of the amount of flammable gas in the sampled air. One such sensor, called a “pellistor” (the name comes from a combination of pellet and resistor), is shown in **Figure 8.16**. It uses the same heater and temperature-sensing mechanism (platinum coil) but uses a palladium catalyst either external to the ceramic bead or embedded in it. The second is better because there is less of a chance of contamination by noncombustible gases (an effect called poisoning, which reduces sensitivity). The advantage of these devices is that they operate at lower temperatures (about 500°C as opposed to about 1000°C for the platinum coil sensor). A sensor of this type will contain two beads, one inert and one sensing bead, the former serving as a reference in the sensing head shown in **Figure 8.17**. The sample of air being tested diffuses through a metal membrane (slowly) and activates the sensor. This generates a reaction in a few seconds. The operation is governed by **Equation (8.9)**, that is, the temperature of the pellistor changes by an amount ΔT depending on the change in enthalpy, but now, because the reaction occurs in air, the specific heat capacity is that of the sensor itself, which tends to be much smaller than that of the gas, that is, the change in temperature is dominated by the reaction and little of the heat is lost into the air during the reaction. This change in temperature changes the resistance of the platinum coil as described in **Equation (3.4)**:

$$R(T) = R(T_0)(1 + \alpha[T - T_0]) \quad [\Omega]. \quad (8.11)$$

The change in resistance is small since the temperature coefficient of resistance (TCR) for platinum is relatively small (see **Table 3.1**), as is the amount of gas sampled.

In common applications, these sensors are used in mines to detect methane and in industry to sense solvents in air. For practical purposes, the most important issue is the concentration at which a flammable gas explodes. This is called the **lower explosive**

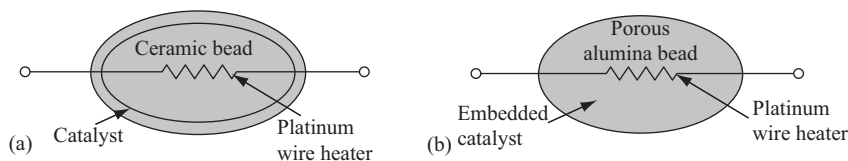


FIGURE 8.16 ■ Catalytic sensors (pellistors). (a) The catalyst is coated on the ceramic bead. (b) The catalyst is embedded in alumina.

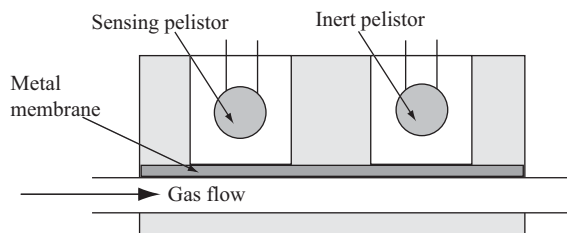


FIGURE 8.17 ■ Construction of a catalytic sensor with a reference sensor using pellistors.

limit (LEL), below which a gas will not ignite. For methane, for example, the LEL limit is 5% (by volume, in air). Thus a methane sensor will be calibrated in percentage of LEL, where 100% LEL corresponds to 5% methane in air.

EXAMPLE 8.7 Detection of carbon monoxide

A pellistor is used to sense CO (assuming a CO-specific ceramic bead is used). The pellistor samples 1 mg of air that contains 1% (by mass) CO. The pellistor operates at a steady-state temperature of 700°C. Its heater is made of platinum and at that temperature has a resistance of 1200 Ω . The TCR of the platinum alloy used is 0.00362/°C at the temperature employed by the sensor. CO has a specific heat capacity of 29 J/mol/K and an enthalpy of combustion in oxygen of 283 kJ/mol. The specific heat capacity of the pellistor itself is 0.750 J/g/K (similar to glass). What is the expected change in resistance of the pellistor due to the combustion of the CO?

Solution: This example shows some of the difficulties involved in this type of calculation. We have the specific heats for both CO and the sensor, but which of them should we use? On top of that, perhaps we should use the specific heat of air. Also, we need to deal with mixed units since the specific heat capacity of the pellistor is, necessarily, given per gram per kelvin. Nevertheless, with a little care and some approximations, meaningful results can be obtained.

First, we note that the fraction of mass sampled is 0.01 mg or 10^{-5} g. We can use $n = 10^{-5}$ in **Equation (8.9)** provided that the enthalpy is written in units of J/g and heat capacity is written in units of J/g/K. In general, gases have a higher heat capacity than most other materials so that the proper quantity to use for the specific heat capacity is that of the pellistor, since it is its temperature that is being raised, whereas the temperature of air changes very little. In any case, CO is a very small fraction of the volume involved. But we need to convert the specific heat capacity to J/g/K. To do so we note that the CO atom is made of one carbon atom and one oxygen atom. The molar mass (MM) of CO is

$$MM(\text{CO}) = 1 \times 12.01 + 1 \times 16 = 28.01 \text{ g.}$$

That is, 1 mole of CO has a mass of 28.01 g. Therefore the enthalpy is

$$\Delta H = 283 \left(\frac{\text{kJ}}{\text{mol}} \right) = \frac{283}{28.01} \left(\frac{\text{kJ}}{\text{g}} \right)$$

Now we can use **Equation (8.9)** with the specific heat of the pellistor to calculate the change in temperature due to combustion of the CO:

$$\Delta T = \frac{\Delta H}{C_p} n = \frac{283 \times 10^3 / 28.01}{0.750} \times 10^{-5} = 0.1347 \text{ K.}$$

The change is small because of the small amount of CO combusted. The change in resistance is

$$R(T) = R(T_0)(1 + \alpha[T - T_0]) = 1200 \times (1 + 0.00362 \times 0.1347) = 1200.585 \Omega.$$

The resistance changes by 0.585 Ω . This is a small change (0.05%), but nevertheless it is measurable.

8.5.3 Thermal Conductivity Sensor

Thermal conductivity sensors do not involve any chemical reaction, but rather use the thermal properties of gases for sensing. A sensor of this type is shown in **Figure 8.18**. It consists of a heater set at a given temperature (around 250°C) in the path of a gas. The heater loses heat to the surrounding area, depending on the gas with which it comes in contact. As the gas concentration increases a larger amount of heat is lost compared to the loss in air, and the temperature of the heater as well as its resistance decreases. This is particularly so with gases that have high thermal conductivities. This change in resistance is sensed and calibrated in terms of gas concentration. Unlike the previous two types of sensors, this sensor is useful for high concentrations of gas. It can be used for inert gases such as nitrogen, argon, and CO₂, as well as for volatile gases, provided of course that the concentration is below the LEL. The sensor is in common use in industry and is a useful tool in gas chromatography in the lab. Based on Fourier's law, it combines the law of heat transfer and Ohm's law in that the heat loss (or gain) of the sensor is sensed through the change in a heated resistor. As with many other sensors, a comparative measurement against a reference sensor, one that is not exposed to the gas being sensed, provides better resolution.

However, the relation between the temperature change and heat loss is relatively complex. Because of that, thermal conductivity sensors must be calibrated, but accurate computation of a sensor's response is difficult and requires specific information for the sensor (dimensions, thermal properties, etc.). Nevertheless, in spite of these difficulties, thermal conductivity sensors exist commercially and are an important tool in the evaluation of gases.

8.6 | OPTICAL CHEMICAL SENSORS

The propagation of light, and in a broader sense that of any electromagnetic radiation in any medium, is governed by the properties of the medium. The transmission, reflection, and absorption (attenuation) of light in a medium, its velocity, and hence its wavelength are dependent on these properties. The optical properties of the medium can all serve as the basis for sensing either by themselves or in conjunction with other transduction mechanisms and sensors. For example, optical smoke detectors use the transmission of light through smoke to detect its presence. Other substances may be sensed in this way, sometimes by adding agents to, for example, color the substance being tested. However, much more complex mechanisms can be used to obtain highly sensitive sensors for a variety of chemical substances and reactions.

In many optical sensors, use is being made of an electrode whose properties change according to the substance being tested. An electrode of this type is called an "optode," a name that parallels the name "electrode" for electrical properties. The optode has an

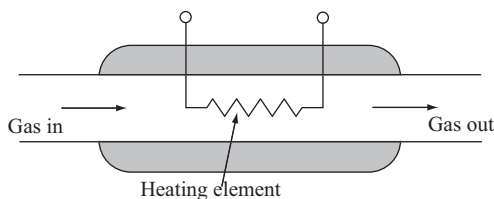


FIGURE 8.18 ■
The construction of a thermal conductivity sensor.

important advantage in that no reference is needed and it is well suited for use with optical guiding systems such as optical fibers.

Other options for optochemical sensing are the properties of some substances to fluoresce or phosphoresce under optical radiation. These chemiluminescence properties can be sensed and used for indications of specific materials or properties. Luminescence can be a highly sensitive method because the luminescence is typically at a different frequency (wavelength) than the frequency (wavelength) of the exciting radiation. Luminescence occurs more often with ultraviolet (UV) radiation, but it can occur in the infrared (IR) or visible range as well, and is often used for detection.

Most optical sensing mechanisms, including luminescence, rely at least in part on the absorption of light by the substance through which it propagates or on which it impinges. This absorption is important in sensors based on the transmission of light and is governed by the Beer–Lambert law, stated as follows:

$$A = \epsilon bM, \quad (8.12)$$

where ϵ is the absorption coefficient characteristic of the medium [$10^3 \text{ cm}^2/\text{mol}$], b is the path length [cm] traveled, and M is the concentration [mol/L]. A is the absorbance $A = \log(P_0/P)$, where P_0 is the incident and P is the transmitted light intensity. This linear relationship only applies to monochromatic radiation.

Perhaps the simplest optochemical sensors are the so-called reflectance sensors, which rely on the reflective properties of a membrane or substance to infer a property of the substance with which it is in contact. In many instances an optical fiber is used as an optical waveguide. The basic structure is shown in **Figure 8.19**. A source of light (LED, white light, laser) generates a beam that is conducted through the optical fiber to the optode. The optical properties of the optode are altered by the substance with which it interacts and the reflected beam is then a function of the concentration of the analyte or its reaction products in the optode. It is also possible to separate the incident and reflected beams by separate optical guides, but usually this is not necessary.

An alternative way of sensing is to use an uncladded optical fiber so some light is lost through the walls of the fiber. This is called an **evanescent loss** and depends on what is in contact with the walls of the fiber. The principle is shown in **Figure 8.20**. In this

FIGURE 8.19 ■
Principle and structure of a reflectance sensor.

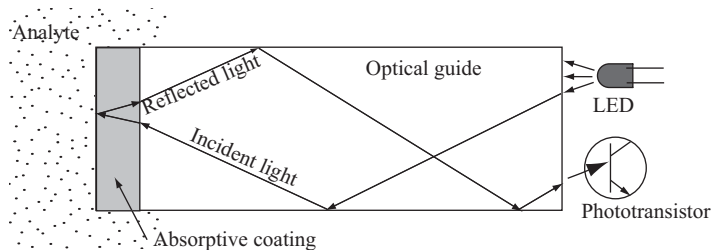
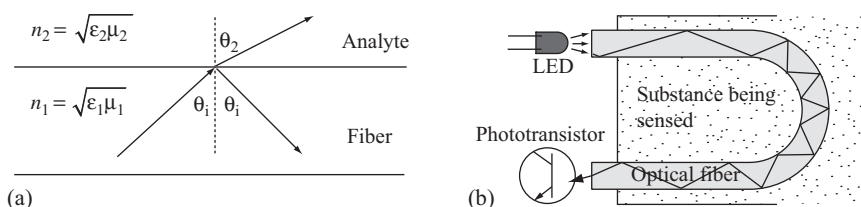


FIGURE 8.20 ■
Evanescent loss sensor. (a) Principle. (b) Structure.



type of sensor the coupling to the analyte is through the walls of the fiber rather than its end. This also means that rather than reflection, the power transmission through the fiber is sensed—a quantity influenced by the power loss through the walls of the fiber. The transmitted wave is then dependent on the amount of light absorbed in the analyte and is therefore a function of the analyte optical properties (primarily the index of refraction) on the surface of the optical fiber. Sensing using this method is based on the transmission properties between a high-permittivity dielectric and a lower-permittivity dielectric such as between glass (or plastic) and air. Given a light wave propagating inside a fiber and impinging from within on the interface between the fiber and analyte, the wave is reflected back into the fiber but part of the power is transmitted across the interface into the analyte. The principle is shown in **Figure 8.20a**. A light beam (a laser beam, for example) is incident on the interface between medium 1 and medium 2 at an angle θ_i . The beam is reflected at the same angle ($\theta_r = \theta_i$). The transmitted (refracted) wave that will penetrate into medium 2 follows from the Snell law of refraction:

$$\frac{\sin \theta_i}{\sin \theta_t} = \frac{n_2}{n_1}, \quad (8.13)$$

where n_1 is the optical index of refraction in medium 1 and n_2 is the optical index of refraction in medium 2. The index of refraction in a dielectric (such as glass or air) is given as

$$n = \sqrt{\epsilon_r \mu_r}, \quad (8.14)$$

where ϵ_r and μ_r are the relative permittivity and relative permeability of the medium, respectively. If the angle of refraction θ_t is equal to or greater than 90° , the wave does not penetrate into medium 2 and is totally contained within medium 1. The critical angle is the incident angle θ_i , for which the refraction angle is 90° , and is given as

$$\theta_i = \sin^{-1} \left(\frac{n_2}{n_1} \right) = \sin^{-1} \sqrt{\frac{\epsilon_{r2} \mu_{r2}}{\epsilon_{r1} \mu_{r1}}}, \text{ provided } \epsilon_{r2} \mu_{r2} < \epsilon_{r1} \mu_{r1}. \quad (8.15)$$

As long as medium 2 has a lower index of refraction, a critical angle exists. The importance of this is that for incident angles larger or equal to the critical angle, all power in the incident wave is reflected back into the volume of the fiber and none is “lost” by propagating into medium 2. Therefore all power is available at the detector (neglecting any possible losses in the fiber itself). At angles of incidence less than the critical angle, the power available at the detector is reduced because of the power transmitted across the interface between the fiber and analyte.

There are two methods that can be used to exploit the critical angle for sensing purposes. The first relies on an increase in the reflected wave power because less power propagates into medium 2, whereas the second does exactly the opposite. To understand this, suppose medium 2 is air and medium 1 is glass. The incident angle is small enough so that the wave penetrates into medium 2, that is, the wave impinges on the surface of the fiber below the critical angle. A portion of the wave is reflected and a portion propagates into air. Now suppose air is replaced with a dielectric such as water vapor or any other substance with a higher permittivity but still satisfying the condition $\epsilon_{r2} \mu_{r2} < \epsilon_{r1} \mu_{r1}$. The index of refraction n_2 increases and less power (or none) propagates into medium 2. Necessarily the proportion of the reflected power increases with the

permittivity of medium 2. Therefore, in this case, the higher the index of refraction of medium 2, the larger the power measured in the reflected wave and a sensor can then be calibrated to sense, for example, relative humidity or the concentration of a substance.

The second method assumes the permittivity of medium 2 is larger than that of the fiber and hence **Equation (8.15)** cannot be satisfied. In that case, the higher the index of refraction of the medium, the lower the reflected power. This method is useful when using the sensor in solutions such as water or when detecting fluids. In practice, the angle of incidence is not a fixed value, but rather a range of angles. Some rays may refract, some not, so that the relation between detected power and the index of refraction is not as simple as the description above. Nevertheless, the output can be calibrated to detect and, to a certain extent, to measure variations in the index of refraction of media on the surface of the sensor.

An evanescent loss sensor capable of detecting and differentiating between various types of fuels (from heavy oil to gasoline) is shown in **Figure 8.21**. It can be used to detect fuel leaks from pumping systems.

pH sensing can be done optically by using special optodes that change color with changes in pH. However, in these systems only about 1 pH unit on either side of the pH of the optode (before the analyte interaction) can be sensed. Although this is a narrow range, it is sufficient for some applications. A sensor of this type is shown in **Figure 8.22**. In this sensor a hydrogen-permeable membrane is used in which phenol red is immobilized on polyacrylamide microspheres. The membrane is a dialysis tube (cellulose acetate) and the optode thus created is attached to the end of an optical fiber. When immersed in the analyte, it diffuses into the optode. Phenol red is known to absorb light at a wavelength of 560 nm (yellow-green light). The amount of light absorbed

FIGURE 8.21 ■

An evanescent loss sensor for detection of fluids. The optical waveguide can be seen at the center of the picture.

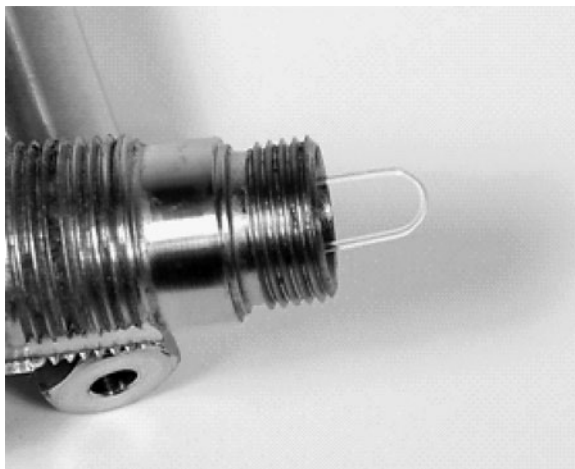
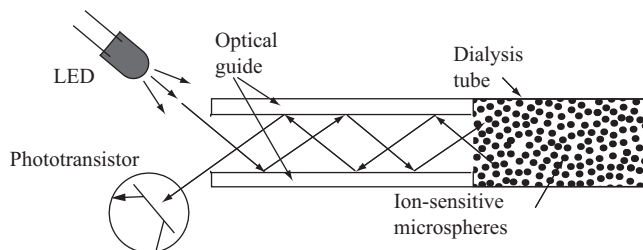


FIGURE 8.22 ■

Structure and principle of an optical pH meter.



depends on the pH and hence the reflected light will change with the pH. The difference between the incident and reflected intensities is then related to pH.

Either the arrangement in **Figure 8.19** or **Figure 8.22** can be used to sense fluorescence. Since fluorescence occurs at different wavelengths than the exciting radiation, the separation between the incident and reflected waves is based on filtering.

A sensor similar to the pH sensor in **Figure 8.22** uses the fluorescent properties of 8-hydroxypyrene-1,3,6-trisulphonic (HPTS), a weak acid. This substance fluoresces when excited by UV light at 405 nm. The intensity of fluorescence is then related to the pH. This material is particularly useful since its normal pH is 7.3, so measurements around the neutral point can be made and, in particular, physiological measurements.

Optodes can also be used to sense ions. Metal ions are particularly easy to sense because they can form highly colored complexes with a variety of reagents. These reagents are embedded in the optode and the reflective properties of the optode–analyte interface are then related to the concentration of the metal ions. Fluorescence is also common in metal ions, a method that is used extensively in analytical chemistry, primarily by use of UV light with fluorescence in the visible range. These methods have been used to sense a variety of ions, including oxygen in water, penicillin, and glucose in blood.

8.7 | MASS SENSORS

Another method of chemical sensing is to detect changes in the mass of a sensing element due to absorption of an analyte. The idea is obvious, but it should be immediately realized that the masses involved in absorption, say, of a gas or water vapor, are minute and a method must be found that is sufficiently sensitive to these minute mass changes. For this reason, mass sensors are also called **microgravimetric** or **micro-balance sensors**. In a practical sensor it is not possible to sense this change in mass directly and therefore indirect methods must be used. This is done by using piezoelectric crystals such as quartz and setting them into oscillation at their resonant frequency (see **Section 7.7**). This resonant frequency is dependent on the way the crystal is cut and on dimensions, but once these have been fixed, any change in mass of the crystal will change its resonant frequency. The sensitivity is generally very high, on the order of 10^{-9} g/Hz and the limit sensitivity is about 10^{-12} g. Since the resonant frequency of crystals can be very high, the change in frequency due to a change in mass is significant and can be accurately measured digitally. As a result, these sensors are highly sensitive and relatively simple. An equivalent approach can be taken with SAW resonators, which are piezoelectric resonators, but because they operate on the propagation of acoustic waves in the piezoelectric material, the wavelengths are shorter and they can resonate at even higher frequencies than crystals resonators (see **Section 7.9**), hence they offer even higher sensitivities.

The shift in resonant frequency of a crystal due to a change in mass Δm can be written as

$$\Delta f = -S_m \Delta m \quad [\text{Hz}], \quad (8.16)$$

where Δf is the change in the resonant frequency, S_m is a sensitivity factor that depends of the crystal (cut, shape, mounting, etc.), and Δm is the change in mass per unit area

(typically given in g/cm^2). The sensitivity factor is given in $\text{Hz}\cdot\text{cm}^2/\mu\text{g}$. Since the sensitivity is more or less constant with the change in mass (for small mass changes), the shift in resonant frequency is linear. On the other hand, the sensitivity factor depends on frequency, so the factors are given for given crystals resonating at given frequencies. Note also that the change in frequency is negative, that is, the frequency decreases as the mass increases. Typical values for the sensitivity factor are $40\text{--}60 \text{ Hz}\cdot\text{cm}^2/\mu\text{g}$.

Equation (8.16) may be written in an inverse form:

$$\Delta m = C_m \Delta f \quad [\text{g}/\text{cm}^2]. \quad (8.17)$$

In this form C_m is a mass factor or mass sensitivity factor and is given in $\text{ng}/\text{Hz}/\text{cm}^2$ and Δm is given in g/cm^2 . Typical values for C_m are $4\text{--}6 \text{ ng}/\text{Hz}/\text{cm}^2$. This form gives the added mass for the measured change in frequency, Δf .

The mass due to the analyte may be absorbed directly into the crystal (or any piezo-electric material) or it may be absorbed in a coating on the crystal. All in all, these are simple and efficient sensors. The main problem is that selectivity is poor since crystals and coatings tend to absorb more than one species, confounding discrimination between species. Also, a basic requirement is that the process be reversible, that is, the absorbed species must be removable (e.g., by heating) without any hysteresis. Although sensors more or less specific to various gases have been developed, the most common is the water vapor sensor.

EXAMPLE 8.8

Sensitivity of a mass sensor

Consider a quartz crystal oscillating at 10 MHz. The crystal is a disk with a diameter of 20 mm. The sensor is used to sense pollen concentrations in air for purposes of warning the public when the pollen count is high. For this purpose the surface of the crystal is coated with a sticky substance to trap pollen particles. Assume that a frequency shift of 100 Hz can be reliably and accurately measured and that the crystal has a mass sensitivity of $4.5 \text{ ng}/\text{Hz}/\text{cm}^2$. On average, a grain of pollen weighs 200 ng. What is the minimum number of pollen grains that can be reliably detected?

Solution: The mass per unit area that can be detected is

$$\Delta m = C_m \Delta f = 4.5 \times 10^{-9} \times 100 = 450 \times 10^{-9} \text{ g}/\text{cm}^2.$$

The area of the sensor is $\pi \times 1^2 = \pi \text{ cm}^2$, so the total mass detectable is

$$\Delta M = \Delta m S = 450 \times 10^{-9} \times \pi = 1413.7 \times 10^{-9} \text{ g}.$$

This is 7 grains of pollen ($1413.7/200 = 7.07$).

Note: Although the values used here are realistic, there are other issues to consider in this type of sensor, including frequency drift with temperature and the frequency stability of the crystal oscillator. These can change the measurement by a few hertz. Typical values are about $5\text{--}10 \text{ Hz}/^\circ\text{C}$, meaning that due to temperature variations alone, the measurement may be off by as much as 10%. At lower sensitivities (larger frequency variations) this may be negligible. If, for example, we were to assume a minimum measurable frequency of 1 kHz, the error would only be 1%, but sensitivity would decrease to 70 grains of pollen. This reduction in sensitivity can be compensated for by allowing a longer collection time. Temperature itself may be controlled quite accurately, reducing the errors in measurement.

8.7.1 Mass Humidity and Gas Sensors

A mass humidity sensor is made by simply coating the resonating crystal with a thin layer of hygroscopic material, which can then absorb water vapor. With hygroscopic coatings and resonators, including SAW resonators, an appropriate medium can be employed since it is not necessary that the crystal itself absorb the vapor. There are many hygroscopic materials that can be used, including polymers, gelatins, silica, and fluorides. The moisture is removed after sensing by heating the absorbing layer. Although a sensor of this type can be quite sensitive, its response time is slow. It may take many seconds (20–30 s) for sensing and many more for regeneration of the sensor (30–50 s).

Nevertheless, the method is useful and has been applied to sensing of a large variety of gases and vapors, some being sensed at room temperatures, some at elevated temperatures. The main difference between sensing one gas and another is in the coating, in an attempt to make the sensor selective. The applications are mostly in sensing of noxious gases and dangerous substances such as mercury. The sensing of SO_2 (mostly due to the burning of coal and fuels) has been accomplished by amine coatings, which react with SO_2 . Concentrations as low as 10 ppb are detectable.

When detecting ammonia (in testing of the environmental effects of wastewater and sewage), the coating is ascorbic acid or pyridoxine hydrochloride (and other similar compounds) with sensitivities down to microgram per kilogram.

Hydrocarbon sulfide is similarly detected by using acetate coatings (silver, copper, and lead acetates are used, as well as others). Mercury vapor is sensed by using gold as a coating, since the two elements form an amalgam that increases the mass of the gold coating. Other applications are in sensing hydrocarbons, nitrotoluenes (emitted by explosives), and gases emitted by pesticides, insecticides, and other sources.

8.7.2 SAW Mass Sensors

The use of crystal resonators has been shown to be a useful and sensitive method of sensing, partly owing to the high frequency of resonance. SAW resonators, based on the use of delay lines (**Section 7.9**), resonate at much higher frequencies and the resonant frequency is highly dependent on the speed of sound in the piezoelectric material. A SAW mass sensor is therefore made as a delay line resonator. The delay line itself is coated with the specific reactive coating for the gas to be sensed. This is shown in **Figure 8.23**. Air containing the gas is sampled (drawn above the membrane) and the resonant frequency measured. The same method can be used to sense solid particles such as pollen or pollutants by replacing the membrane with a sticky substance. Of course, the problem then is regeneration—cleaning the surface for the next sampling.

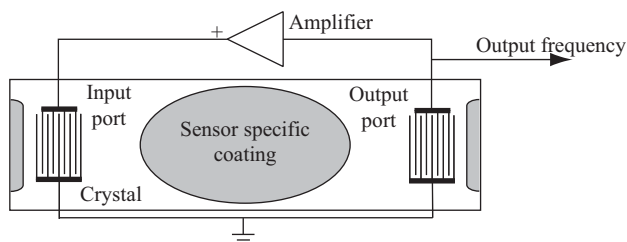


FIGURE 8.23 ■ A SAW mass sensor based on a delay line oscillator. Output frequency is related to the mass of the coating.

TABLE 8.1 ■ Some sensed substances and the coatings used for that purpose

Compound	Chemical coating	SAW material
SO ₂	TEA (triethanolamine)	Lithium niobate
H ₂	Pd (palladium)	Lithium niobate, silicon
NH ₃	Pt (plutonium)	Quartz
H ₂ S	WO (Wolfram oxide)	Lithium niobate
Water vapor	Hygroscopic material	Lithium niobate
NO ₂	PC (phthalocyanine)	Lithium niobate, quartz
NO ₂ , NH ₃ , SO ₂ , CH ₄	PC (phthalocyanine)	Lithium niobate
Explosives vapor, drugs	Polymer	Quartz
SO ₂ , methane	None	Lithium niobate

Some sensors of this type are thus single-use sensors. As was the case with crystal microbalance sensors, the choice of coating determines the selectivity of the sensor. **Table 8.1** shows some sensed substances and the appropriate coatings.

The sensitivities of SAW resonators can be much higher than those of crystal resonators, with limit sensitivities of approximately 10^{-15} g. Sensitivities expected are on the order of 50 $\mu\text{Hz/Hz}$. This means that for a 500 MHz resonator, the frequency shift sensitivity is 25 kHz. This is more than sufficient for accurate sensing.

8.8 | HUMIDITY AND MOISTURE SENSORS

The use of a mass sensor to sense humidity has been described previously and the extension of this method to SAW sensors is indicated in **Table 8.1**. There are other methods of sensing humidity, but all involve some type of hygroscopic medium to absorb water vapor. These can take many forms, of which capacitive, conductive, and optical are the most common.

The terms humidity and moisture are not interchangeable. Humidity refers to the water content in gases, such as in the atmosphere. Moisture is the water content in any solid or liquid. Other important, related quantities are the dew point temperature, absolute humidity, and relative humidity. These are defined as follows:

Absolute humidity is the mass of water vapor per unit volume of wet gas, expressed in g/m^3 .

Relative humidity is the ratio of the water vapor pressure of the gas (usually air) to the maximum saturation water vapor pressure in the same gas at the same temperature. Saturation is the water vapor pressure at which droplets form. The atmospheric pressure is the sum of the water vapor pressure and the dry air pressure. However, relative humidity is not used above the boiling point of water (100°C) since the maximum saturation above that temperature changes with temperature.

Dew point temperature is the temperature at which relative humidity is 100%. This is the temperature at which air can hold the maximum amount of moisture. Cooling below it creates fog (water droplets), dew, or frost.

8.8.1 Capacitive Moisture Sensors

The simplest moisture sensor is the capacitive sensor since it simply relies on the change in permittivity due to moisture. The permittivity of water is rather high ($80\varepsilon_0$ at low frequencies). Humidity is different than liquid water, and hence the permittivity of humid air is either given in tables as a function of relative humidity or can be calculated from the following empirical relation:

$$\varepsilon = \left(1 + \frac{1.5826}{T} \left(P_{ma} + \frac{0.36P_{ws}}{T} RH \right) 10^{-6} \right) \varepsilon_0 \quad [\text{F/m}], \quad (8.18)$$

where ε_0 is the permittivity of vacuum, T is the absolute temperature [K], P_{ma} is the pressure of moist air [Pa], RH is the relative humidity [%], and P_{ws} is the pressure of saturated water vapor pressure [Pa] at the temperature T . These quantities may seem a bit confusing. The pressure of moist air is the partial pressure exerted by water vapor in the atmosphere. It is temperature dependent and reaches the ambient pressure at 100°C (that's the reason water boils at 100°C). Saturated water vapor pressure is the water vapor pressure at 100% humidity, and is also temperature dependent. Both of these quantities can be calculated and are available in tables. The pressure of saturated water vapor and the pressure of moist air can be calculated from the following experimental formulas:

$$P_{ws} = 133.322 \times 10^{0.66077+7.5t/(237.3+t)} \quad [\text{Pa}] \quad (8.19)$$

$$P_{ma} = 133.322e^{20.386-5132/(t+273.15)} \quad [\text{Pa}], \quad (8.20)$$

where t is given in $^\circ\text{C}$ and P_{ws} in Pa.

The capacitance of a parallel plate capacitor is $C = \varepsilon A/d$, and this then establishes a relation between capacitance and relative humidity (A is the area of the capacitor, d is the distance between the plates, and ε is the permittivity of the substance between the plates):

$$C = C_0 + C_0 \frac{1.5826P_{ma}}{T} 10^{-6} + C_0 \frac{75.966P_{ws}}{T} 10^{-6} RH \quad [\text{F}], \quad (8.21)$$

where C_0 is the capacitance of the capacitor in vacuum ($C_0 = \varepsilon_0 A/d$). This relation is linear at any given temperature. The pressure of moist air adds a fixed component, whereas the variable component is entirely due to humidity. However, for a practical capacitor, the capacitance is rather small (the capacitor plates cannot be too large for practical reasons and the distance between the plates must be reasonable—at least a few micrometers—to allow air motion). In practical designs, means of increasing this capacitance are used. One approach is to use a hygroscopic material between the plates, both to increase the capacitance at no humidity and to absorb the water vapor. These materials can be hygroscopic polymer films. The metal plates can be made of gold. In a device of this type the capacitance can be approximated as

$$C = C_0 + C_0 \alpha_h H \quad [\text{F}], \quad (8.22)$$

where α_h is a moisture coefficient. α_h is not necessarily constant, and in general may depend on temperature and on the relative humidity itself. This method assumes that the moisture content in the hygroscopic polymer is directly proportional to relative humidity

and that as the humidity changes, the moisture content changes (i.e., the film does not retain water). Under these conditions the sensing is continuous, but, as expected, changes are slow and the sensor's output necessarily lags behind, especially if changes in moisture are quick. A sensor of this type can sense relative humidity from about 5% to 90% at an accuracy of 2%–3%.

EXAMPLE 8.9 Capacitive relative humidity sensor

A capacitive relative humidity sensor using a hygroscopic polymer is given. To evaluate its properties, the capacitance is measured at 20% RH and at 80% RH. The results are $C = 448.4$ pF at 20% RH and $C = 491.6$ pF at 80% RH. The capacitor is a simple parallel plate capacitor.

- Calculate the moisture coefficient of the sensor, its output full scale (OFS), and its sensitivity.
- Calculate the range of relative permittivities of the sensor for the OFS in (a).

Solution: Using **Equation (8.22)** we can determine the dry capacitance C_0 (i.e., the capacitance at zero relative humidity) and the moisture coefficient. Then using the formula for the parallel plate capacitor, the permittivity is calculated directly.

- At 20% RH

$$448.4 = C_0 + \alpha C_0 \times 20 \text{ pF}$$

and at 80% RH

$$491.6 = C_0 + \alpha C_0 \times 80 \text{ pF.}$$

Subtracting the first relation from the second:

$$491.6 - 448.4 = \alpha C_0 \times (80 - 20) \rightarrow 43.2 = \alpha C_0 \times 60 \rightarrow \alpha C_0 = \frac{60}{43.2} = 1.3889.$$

Substituting this back into the first relation:

$$448.4 = C_0 + 1.3889 \times 20 \rightarrow C_0 = 448.4 - 1.3889 \times 20 = 420.62 \text{ pF.}$$

The moisture coefficient is

$$\alpha C_0 = 1.3889 \rightarrow \alpha = \frac{1.3889}{C_0} = \frac{1.3889}{420.62} = 0.003302.$$

The OFS is the capacitance of the sensor for the input full scale (IFS). Necessarily the IFS is 0%–100%. The relation for capacitance is

$$C = 420.62 + 1.3889H \quad [\text{pF}].$$

At 0% RH we already obtained $C = C_0 = 420.62$ pF. At 100% RH we have

$$C = 420.62 + 1.3889 \times 100 = 559.51 \text{ pF.}$$

That is, the OFS is 420.62 pF to 559.51 pF, or 138.89 pF.

Since the output is linear, it suffices to divide the OFS by the IFS to obtain the sensitivity. In this case this is 1.3889 pF/% RH.

b. The permittivity is calculated from the capacitance of a parallel plate capacitor. We write

$$C = \epsilon \frac{A}{d} \quad [\text{F}].$$

Because we do not know the plate area or the distance between them, we calculate the ratio A/d from the empty capacitor:

$$\frac{A}{d} = \frac{C_0}{\epsilon_0} = \frac{429.88 \times 10^{-12}}{8.854 \times 10^{-12}} = 45.552 \text{ m}.$$

This ratio remains the same no matter what the relative humidity is. At 100% humidity, the capacitance is 522.47 pF and the permittivity is

$$\epsilon = \frac{C}{A/d} = \frac{522.47 \times 10^{-12}}{45.552} = 11.4697 \times 10^{-12} \text{ F/m}.$$

The relative permittivity is

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} = \frac{11.4697 \times 10^{-12}}{8.854 \times 10^{-12}} = 1.2954.$$

The relative permittivity varies from 1 to 1.2954. This is a reasonably large change (almost 30%) in relative permittivity as humidity varies from 0% to 100%.

One of the difficulties with parallel plate capacitor humidity sensors is that the hygroscopic film must be thin and moisture can only penetrate from the sides. They are therefore slow to respond to changes in moisture because of the time it takes for moisture to penetrate throughout the film. A different approach is shown in **Figure 8.24**. Here the capacitor is flat and built from a series of interdigitated electrodes to increase capacitance. The hygroscopic dielectric may be made of SiO_2 or phosphosilicate glass. The layer is very thin to improve response. Because the sensor is based on silicon, temperature sensors are easily incorporated to allow for compensation, as are other components such as oscillators. The capacitance of the device is low and therefore it will normally be used as part of an oscillator and the frequency sensed. However, the permittivity of the dielectric is frequency dependent (goes down with frequency). This means that the frequency cannot be too high, especially if low humidity levels are sensed.

8.8.2 Resistive Humidity Sensor

Humidity is known to change the resistivity (conductivity) of some materials. This can be used to build resistive relative humidity sensors. To do so, a hygroscopic conducting layer and two electrodes are provided. Often the electrodes will be interdigitated to

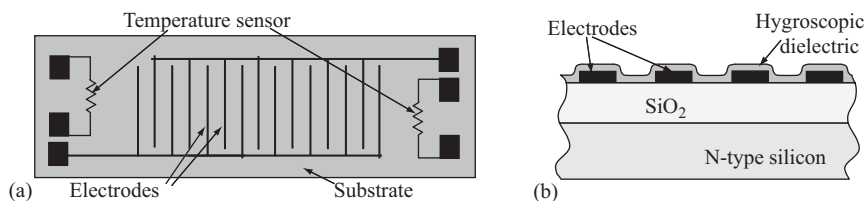


FIGURE 8.24 ■
A capacitive sensor with interdigitated electrodes.

increase the contact area, as shown in **Figure 8.25**. The hygroscopic conductive layer must have a relatively high resistance, which decreases with humidity (actually absorbed moisture). There are some materials that can be used for this purpose, including polystyrene treated with sulfuric acid and solid polyelectrolytes, but a better structure is shown in **Figure 8.26**. It operates as above but the base material is silicon. An aluminum layer is formed on the silicon (highly doped so its resistivity is low). The aluminum layer is oxidized to form a layer of Al_2O_3 , which is porous and hygroscopic and has a low conductivity that increases with relative humidity. An electrode of porous gold is deposited on top to create the second contact and to allow moisture absorption in the Al_2O_3 layer. The resistance between the upper gold electrode and the substrate electrode is then a measure of relative humidity.

8.8.3 Thermal Conduction Moisture Sensors

Humidity may also be measured through thermal conduction, as higher humidity will increase thermal conduction. This sensor senses absolute humidity rather than relative humidity. The sensor makes use of two thermistors connected in a differential or bridge connection (bridge connection is shown in **Figure 8.27a**). The thermistors are heated to an identical temperature by the current through them so that the differential output is zero in dry air. One thermistor is kept in an enclosed chamber as a reference and its resistance is constant. The other is exposed to air and its temperature changes with humidity. As humidity increases, the thermistor temperature decreases and hence its resistance

FIGURE 8.25 ■
A humidity sensor based on the interdigitated electrode capacitor.

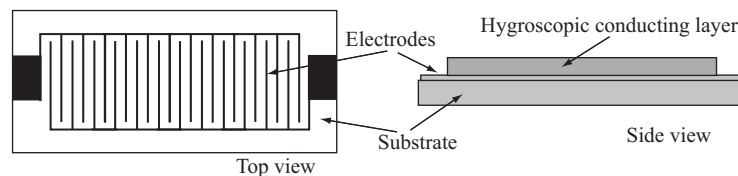


FIGURE 8.26 ■
A porous (hygroscopic) layer humidity sensor.

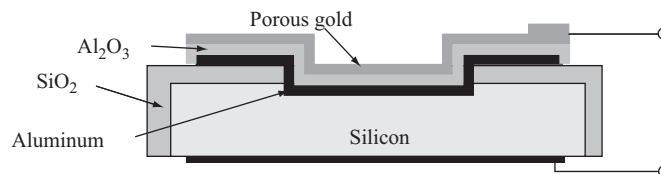
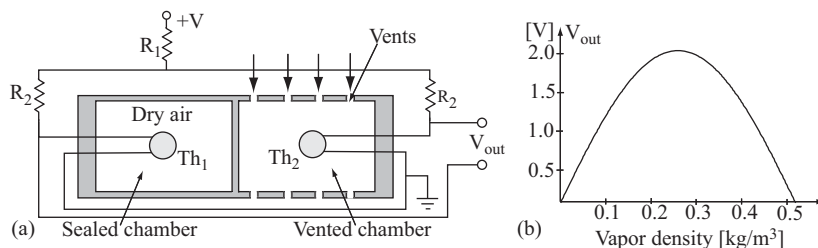


FIGURE 8.27 ■
A thermal conductivity moisture sensor.
(a) Structure.
(b) Response.



increases (for NTC thermistors). At saturation the peak resistance is reached, beyond which the output drops again as the thermal conductivity decreases (**Figure 8.27b**).

8.8.4 Optical Humidity Sensor

By far the most accurate humidity sensing method is optical and is based on duplicating the dew point by regulating the temperature of a mirror. When the dew point is reached, the relative humidity is 100%. The relative humidity (RH) is obtainable from the dew point temperature and the saturation water vapor pressure relation:

$$DPT = \frac{237.3 \left(0.66077 - \log_{10} \left(\frac{P_{ws} \cdot RH/100}{133.322} \right) \right)}{\log_{10} \left(\frac{P_{ws} \cdot RH/100}{133.322} \right) - 8.16077}, \quad (8.23)$$

where P_{ws} [Pa] is the saturation water vapor pressure given in **Equation (8.19)**.

It should be noted that the higher the relative humidity at any temperature, the higher the dew point temperature until, at 100% relative humidity, the dew point temperature equals the temperature of the air (see **Example 8.10**). By measuring the ambient temperature t and then evaluating the dew point temperature (DPT), the relative humidity (RH) can be calculated from **Equation (8.23)**. Thus the basic idea is to use a dew point sensor built as shown in **Figure 8.28**. The sensor is based on detecting the dew point on the surface of a mirror. To do so, light is reflected off the mirror and the light intensity monitored. A Peltier cell is used to cool the mirror to its dew point. When the dew point temperature is reached, the controller keeps the mirror at the dew point temperature by regulating the current in the Peltier cell. The reflectivity of the mirror decreases since water droplets form on the mirror (the mirror fogs up). This temperature is measured and is the dew point temperature in **Equation (8.23)**. Although this is a rather complex sensor and includes a reference cell (which is kept at the same temperature) for balancing, it is very accurate, capable of sensing the dew point temperature at accuracies of less than 0.05°C .

The same measurement can be done with the crystal microbalance sensor described in the previous section. In that case, the resonant frequency of a crystal covered with a water-selective coating is used and its resonant frequency sensed while the sensor is cooled. At the dew point, the sensor's coating is saturated and the frequency drops to its lowest value. Equally well, a SAW mass sensor can be used with even greater accuracy. The heating/cooling is achieved as in **Figure 8.28** by use of a Peltier cell.

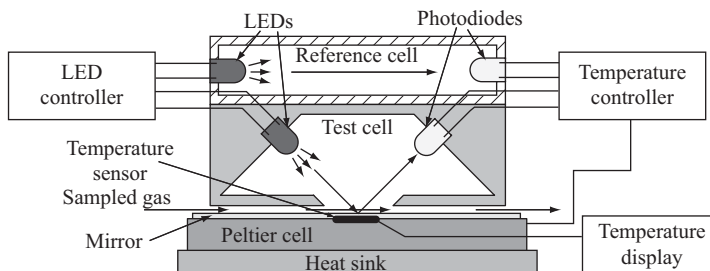


FIGURE 8.28 ■ An optical dew point sensor based on measurement of the dew point.

EXAMPLE 8.10 Calculation of dew point temperature

Calculate the dew point temperature in air at 60% relative humidity at 25°C. Show that at 100% humidity, the dew point temperature must equal the ambient temperature of 25°C.

Solution: The saturation water vapor is calculated first from **Equation (8.19)** as follows:

$$P_{ws} = 133.322 \times 10^{0.66077 + 7.5t/(237+25)} = 3165.94 \text{ Pa.}$$

The dew point temperature is calculated from **Equation (8.23)**:

$$\begin{aligned} DPT &= \frac{237.3 \left(0.66077 - \log_{10} \left(\frac{P_{ws} \cdot RH/100}{133.322} \right) \right)}{\log_{10} \left(\frac{P_{ws} \cdot RH/100}{133.322} \right) - 8.16077} \\ &= \frac{237.3 \times \left(0.66077 - \log_{10} \left(\frac{3165.94 \times 60/100}{133.322} \right) \right)}{\log_{10} \left(\frac{3165.94 \times 60/100}{133.322} \right) - 8.16077} \\ &= 16.69^\circ\text{C.} \end{aligned}$$

That is, water droplets (condensation) will form at any temperature below 16.69°C.

At 100% humidity we get

$$\begin{aligned} DPT &= \frac{237.3 \left(0.66077 - \log_{10} \left(\frac{3165.94 \times 100/100}{133.322} \right) \right)}{\log_{10} \left(\frac{3165.94 \times 100/100}{133.322} \right) - 8.16077} \\ &= 25.0^\circ\text{C} \end{aligned}$$

as expected.

EXAMPLE 8.11 Absolute humidity sensor

Humidity is intricately linked with temperature and pressure and any attempt at sensing humidity must, at the very least, take these into account. However, given the pressure and temperature, measurement of humidity can be relatively simple. Consider the measurement of absolute humidity (amount of water) in air using a capacitive sensor. At 30°C and 1 atm of pressure, the amount of water in air varies between 0 and 30 g/m³. Given a parallel plate capacitor with a plate area of 10 cm² and separation between the plates of 0.01 mm, estimate the range of capacitance of the sensor.

Solution: As the humidity increases, the relative permittivity of air increases. The relative permittivity of water at that temperature is approximately 80, whereas the relative permittivity of air is 1. One way to estimate the permittivity of the mixture is to use a volume average, as follows:

$$\epsilon_r = \frac{\epsilon_{rw} \times v_w + \epsilon_{ra} \times v_a}{v_w + v_a} = \frac{80 \times 30 + 1 \times 10^6}{10^6} = 1.0024,$$

where 30 g of water was taken as 30 cL in volume and 1 m^3 of air is 10^6 cL. ϵ_{rw} is the relative permittivity of water, ϵ_{ra} is the relative permittivity of air, v_w is the volume of water, and v_a is the volume of air.

The relative permittivity varies between 1 (no moisture) and 1.0024 when the air is saturated. In terms of capacitance (see **Equation (5.2)**),

$$C_{\max} = \frac{\epsilon_0 \epsilon_r S}{d} = \frac{8.854 \times 10^{-12} \times 1.0024 \times 10 \times 10^{-4}}{0.01 \times 10^{-3}} = 8.875 \times 10^{-10} \text{ F}$$

and

$$C_{\min} = \frac{\epsilon_0 \epsilon_r S}{d} = \frac{8.854 \times 10^{-12} \times 1 \times 10 \times 10^{-4}}{0.01 \times 10^{-3}} = 8.854 \times 10^{-10} \text{ F},$$

where S is the area of each plate and d is the separation between them. ϵ_0 is the permittivity of vacuum. The capacitance changes between 885.4 pF and 887.5 pF. This is a small change (about 0.34%), but nevertheless it is measurable, especially if the capacitor is part of an oscillator and the frequency is measured (see **Chapter 11**). The change in capacitance can be increased by adding a hygroscopic material between the plates, but the advantage of the simple capacitor is that its response is faster and one does not have to worry about “drying” the hygroscopic material before measurements. It is also obvious from this example why this type of sensor is not the best—the change in capacitance is small and, since that depends on pressure and temperature, sensing is likely to be inaccurate.

8.9 | CHEMICAL ACTUATION

Chemical actuation can take many forms. The most obvious is a chemical reaction whose purpose is to affect an outcome. But even here there are many forms of reactions that are being used. One type of reaction is the conversion or oxidation processes that take place in the catalytic converter of a vehicle. The purpose, of course, is to reduce polluting constituents in the exhaust stream. Another type is the explosive inflation of an airbag. Although one may argue that this is a purely mechanical action, it is in fact the explosion of a charge that generates sufficient gas, sufficiently fast for the airbag system to be effective. And the whole idea of the internal combustion engine is based on what can be properly called chemical actuation, where the combustion converts hydrocarbons into gases (mostly CO_2 , but also CO , NO_x , and SO_4 , of which only CO_2 is considered a nonpollutant). A third example of chemical actuation is the electroplating process and cell.

There are many more chemical actuators, including chemical scrubbers, galvanic cells (batteries), and electrolytic cells, but we will concentrate here on only four: the catalytic converter, the airbag or explosive actuator, electroplating, and cathodic protection against corrosion.

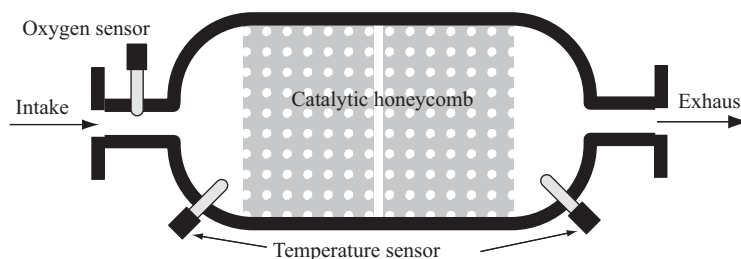
8.9.1 The Catalytic Converter

The catalytic converter as used in vehicles has become one of the primary tools in pollution control and is universally used in gasoline fueled cars. With some modifications it is also applicable to diesel vehicles. The catalytic converter is used for three purposes:

1. Oxidation of CO to CO_2 to reduce the presence of this pollutant in air:



FIGURE 8.29 ■ The catalytic converter.



2. Oxidation of unburned hydrocarbons (HCs) to (CO₂) and water (H₂O):



3. Reduction of nitrogen oxides (NO and NO₂, together referred to as NO_x) to free nitrogen and oxygen:



These pollutants are produced either through incomplete combustion (CO) or as a high-temperature reaction (NO_x). The catalytic converter also produces by-products, including hydrogen sulfide (H₂S) and ammonia (NH₃). H₂S is controlled through the reduction of sulfur in gasoline and by the catalytic converter to eliminate by-products.

The converter is actually quite simple. It is a chamber enclosing a honeycomb structure made of Al₂O₃ or a mesh structure to increase surface contact with the exhaust gases. The structure is coated with a catalyst, typically platinum (but other catalysts such as palladium, rhodium, cerium, manganese, and nickel may be used for specific purposes). The whole structure is heated to a temperature between 600°C and 800°C by the exhaust gases. The catalyst only stimulates the chemical reaction, it does not take part in it. For this to happen the converter must first reach a minimum temperature (400°C–600°C). Beyond that the efficiency increases until at normal operating temperatures it reaches 90% or higher. The basic structure is shown in **Figure 8.29**, which also shows temperature sensors and at least one oxygen sensor. The oxygen sensor is necessary to control the reaction since oxygen in sufficient quantities must be present for the conversion to occur. This is supplied through the combustion process by increasing or decreasing the amount of oxygen in the mixture. The temperature sensors monitor the operation of the converter. For example, as CO oxidizes, the temperature increases, showing a higher temperature at the exhaust of the converter.

EXAMPLE 8.12

Overheating of catalytic converters

The catalytic converter in a car can overheat or even melt due to excess heat produced by the reactions occurring in it. Specifically, the conversion of CO produces additional heat that elevates the temperature of the converter. If the engine produces large quantities of CO (due to incomplete burning of fuel), the catalytic converter may suffer permanent damage. To understand this better consider a four-stroke, six-cylinder, internal combustion engine with a total displacement of 2400 cc running at 2000 rpm. Typical concentrations of CO in the exhaust of an engine before the catalytic converter are about 5000 ppm, whereas after the catalytic converter they drop to less

than 100 ppm. Estimate the heat generated from the conversion of CO to CO₂ in the catalytic converter of the engine per minute. The density of air is 1.2 kg/m³ (at 20°C) and the properties of CO are a specific heat capacity of 29 J/mol/K and an enthalpy of combustion in oxygen of 283 kJ/mol.

Solution: The total mass of gasses in the exhaust equals the air mass plus the mass of the fuel. Since the mass of fuel is rather small compared with the air mass, we shall neglect it in this calculation. We first calculate the mass of the air and then estimate the molar mass of the CO being converted.

The displacement of an engine is the volume of all of its cylinders, and each cylinder has a displacement volume of 400 cc. In a four-stroke engine, one cylinder is filled each half-rotation, so that all four cylinders are filled in two rotations. That is, the engine takes in 1.2 L of air per rotation or $1.2 \times 2000 = 2400$ L/min. This translates into $2400/1000 = 2.4$ m³, or a mass of $2.4 \times 1.2 = 2.88$ kg of air per minute. Note that since the mass of fuel consumed per minute is only about 10 g, its contribution to the total exhaust mass is small. The concentration of CO is 5000 ppm, meaning that the mass of CO in the exhaust is

$$Mass_{CO} = 2.88 \times 5,000 \times 10^{-6} = 0.01414 \text{ kg/min,}$$

or 14.14 g/min. The molar mass of CO is (see **Example 8.7**)

$$MM(CO) = 1 \times 12.01 + 1 \times 16 = 28.01 \text{ g.}$$

That is, 1 mole of CO has a mass of 28.01 g. Therefore the heat generated per minute is

$$H = 283 \times \frac{14.14}{28.01} = 142.864 \text{ kJ.}$$

The conversion generates about 143 kJ of heat.

This heat raises the temperature of the catalytic converter. The change in temperature can be calculated given the thermal properties of the converter and ambient temperature. In a car that is a difficult task, since air motion as the car moves changes the conditions dynamically. Nevertheless, this is a concern, and high levels of CO can lead to overheating of the converter and its possible failure.

8.9.2 The Airbag

The airbag system in vehicles is used as a safety device to protect occupants in case of collision. A number of sensors (accelerometers, wheel speed sensors, impact sensors, and others) are monitored to determine if a collision occurred and the airbag needs to be deployed. A small explosive charge is set electrically that then initiates the reaction and starts the gas-generation process. A variety of materials have been and are being used, but most of them release nitrogen as the primary gas. For example, in early systems, sodium azide (NaN₃) was used as a propellant. When ignited it produces sodium and nitrogen:



There are other propellants that are less toxic, some are organic, some inorganic, and some airbag systems use compressed nitrogen or argon for the same purpose. Some of the alternatives are triazole (C₂H₃N₃), tetrazole (CH₂N₂), nitroguanidine (CH₄N₄O₂),

nitrocellulose ($\text{C}_6\text{N}_7(\text{NO}_2)_3\text{O}_5$), and others, usually with stabilizers and reaction modifiers added to increase stability over time and to control the rate of the reaction (many of these materials are explosives and unstable, hence the need for additives). A typical airbag will contain between 50 and 150 g of propellant depending on the volume of the airbag. This generates a high volume of nitrogen that allows fast inflation of the bag and sufficient pressure to absorb the impact of the body.

EXAMPLE 8.13**Inflation of an airbag**

Estimate the pressure in an airbag that uses 100 g of NaNH_2 , assuming the airbag has a volume of 50 L. Assume as well that the temperature of the gas increases to 50°C and that no gas escapes from the airbag. Naturally not all these conditions are satisfied in reality, but they allow an estimate of the process. For example, the airbag has vents to deflate the gas, but the inflation is so fast that initially the approximation here is valid.

Solution: From the reaction in **Equations (8.27)**, 2 moles of NaNH_2 generates 3 moles of nitrogen. At standard temperature and pressure (STP) a mole of gas (any gas) is 22.4 L. Thus we need to calculate the number of moles generated and for that we must evaluate the molar mass of NaNH_2 . Using the periodic table we write

$$MM = 22.9897 + 3 \times 14.0067 = 65.0099 \text{ g/mol.}$$

Thus 100 g of NaNH_2 will produce n moles:

$$n = \frac{100}{65.0099} = 1.5382 \text{ mol.}$$

However, since 2 moles of NaNH_2 produces 3 moles of nitrogen gas, n must be multiplied by $3/2$. Now we can use the ideal gas relation as follows:

$$PV = nRT,$$

where P is pressure [N/m²], V is volume [m³], n is the number of moles, R is the gas constant, equal to 8.3144621 J/mol/K, and T is the temperature [K]. The pressure inside the bag is therefore

$$P = \frac{nRT}{V} = \frac{1.5382 \times 1.5 \times 8.3144621 \times 323.15}{0.050} = 123,988 \text{ N/m}^2.$$

This pressure is somewhat low. Airbags for adults require a pressure of about 150–200 kPa.

Notes: The temperature used here is an estimated value and, because the pressure builds up quickly, it may not be uniform within the bag and may be higher. The bag deflates through vents in about 2 s. The inflation time is typically 40–50 ms.

8.9.3 Electroplating

Electroplating is an electrodeposition process through which a metal is coated with a thin layer of another metal to affect a desired property. In many cases this deposition is decorative, in others it is protective, and in still others it may be structural. In effect, metal ions in a solution are moved by means of an electric field from the solution to the

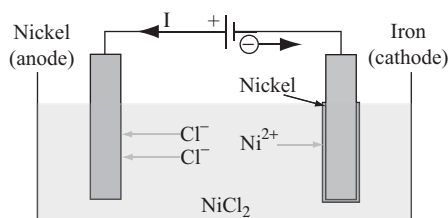


FIGURE 8.30 ■
Electroplating of
nickel on iron.

medium being coated. To maintain the process, a sacrificial electrode of the metal used for coating is usually (but not always) used to supply the ions. The process, in its simplest form, is shown in **Figure 8.30**. In this case an iron piece connected as the cathode is coated with nickel. The electrolyte is usually an aqueous solution of a salt of the metal used for coating. In the case shown here the solution is nickel chloride (NiCl_2) and the anode is nickel to supply the ions. The NiCl_2 ionizes in water to nickel cations (ions with excess protons or positive ions; Ni^{2+}) and chlorine anions (ions with excess electrons or negative ions; Cl^{1-}). When the cations reach the cathode they reduce to metallic nickel by gaining two electrons. At the same time, the chlorine anions give up their electron and reduce to chlorine. This is released as gas at the anode. The role of DC is particularly important in the process. First, the metal mass being electroplated is directly proportional to the current since the extra electrons needed for reduction are supplied by the current. This is usually stated through Faraday's law as follows:

1. The mass of the metal coating is proportional to the quantity of electricity passed through the cell, and
2. The mass of the material liberated is proportional to its electrochemical equivalent. This can be stated as follows:

$$W = \frac{Ita}{nF} \quad [\text{g}], \quad (8.28)$$

where W is the mass [g], I is the current [A], t is time [s], a is the atomic weight of the metal, n is the valence of the dissolved metal [g-eq/mole], and $F = 96,485.309 \text{ C/g-eq}$ is Faraday's constant. In this particular case $n = 2$ (the reduction requires two electrons). Faraday's constant means that to deposit 1 g of metal one needs a charge equal to nF coulombs ($\text{A} \cdot \text{s}$). This charge is supplied by the current over time. Faraday's constant also indicates one specific problem with electroplating: it requires very large currents or, alternatively, it can be a very slow process. The voltages used are typically low, on the order of only a few volts, but nevertheless the energy needed is significant.

There are many variations of the basic process and many different solutions are used, each with its own properties and each adapted for a particular use, but these issues are more technological than fundamental. For example, in gold plating one does not use a sacrificial gold anode, but rather a carbon or lead anode. All ions are supplied by the solution (usually a gold-cyanide solution) and this solution must be replenished to sustain the plating process. Depending on the materials used, the process may release gases, some of which need to be processed and may produce dangerous substances that again need to be treated properly.

Electroplating is a common process in use since the very discovery of the electric cell by Alessandro Volta in 1800. It was first reported in 1805 following Volta's invention, but there is some intriguing speculation that the process was known in ancient times.

EXAMPLE 8.14 Gold plating of printed circuit board traces

Printed circuit boards are made of copper over fiberglass, but certain parts are often gold plated to improve contact and prevent corrosion. These include connector traces and pads. To get an idea of the issues involved, consider the plating of a printed circuit board on which a total of 8 cm^2 are gold plated to a thickness of $25 \text{ }\mu\text{m}$. Plating is done in a gold-cyanide solution, $\text{Au}(\text{Cn})_2^{-1}$, at a relatively low current density of 10^4 A/m^2 to ensure a smooth coating. The gold-cyanide ion dissociates into a gold cation (Au^+) and two anions (2Cn^-). Calculate the time needed for plating.

Solution: In this case the reduction requires a single electron, $n = 1$. The atomic weight of gold is $a = 196.966543$. The total mass that needs to be plated is calculated from the volume needed and the atomic mass. The volume is

$$\text{vol} = \text{area} \times \text{thickness} = 8 \times 10^{-4} \times 25 \times 10^{-6} = 2 \times 10^{-8} \text{ m}^3.$$

The density of gold is $19,320 \text{ kg/m}^3$. Therefore the mass is

$$M = \text{vol} \times \text{density} = 2 \times 10^{-8} \times 19320 = 3.864 \times 10^{-4} \text{ kg}.$$

Equation (8.28) requires the mass in grams. The total mass needed is 0.3864 g . The current needed is the given current density multiplied by the area being plated:

$$I = \text{area} \times \text{current density} = 8 \times 10^{-4} \times 10^4 = 8 \text{ A}.$$

The time needed is found from **Equation (8.28)**:

$$t = \frac{nFW}{Ia} = \frac{1 \times 96,485.309 \times 0.3864}{8 \times 197} = 23.66 \text{ s}.$$

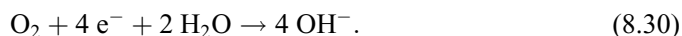
It takes just under 24 s to affect the plating.

8.9.4 Cathodic Protection

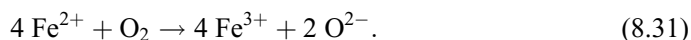
Corrosion of metals occurs when the metal transfers electrons in the presence of oxygen, starting a reaction that ends in any of a number of corrosion products. The best known of these products is iron oxide (Fe_2O_3), but other products exist and are quite common. The reactions are facilitated by the presence of water and oxygen and accelerated by acids. Therefore one can say that corrosion takes place in an electrolytic cell. The reactions that lead to the formation of Fe_2O_3 (rust) are as follows: iron oxidizes in the presence of oxygen by transferring electrons to oxygen,



If water is present, the excess electrons, oxygen, and water form hydroxide ions:



The iron ions react with oxygen:



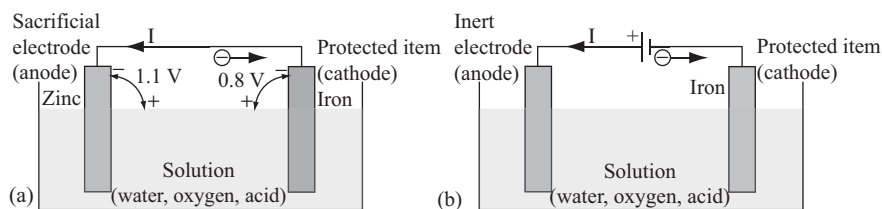
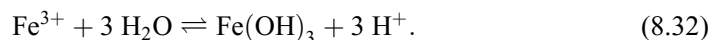
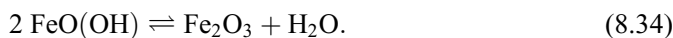
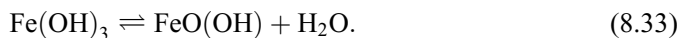


FIGURE 8.31 ■ Cathodic protection. (a) Passive or sacrificial cathodic protection. (b) Active or impressed current cathodic protection.

The reaction that leads to the formation of Fe_2O_3 is



The $\text{Fe}(\text{OH})_3$ product dehydrates and leads to the formation of Fe_2O_3 as follows:



As mentioned, there are many iron corrosion products whose formation depends on the availability of oxygen and water as well as other salts and acids.

Protection against corrosion, short of preventing contact with water and oxygen (through paints, coatings, or plating), must eliminate the oxidation of iron. That is, if one can prevent the transfer of electrons from iron to oxygen, the process stops and iron is protected against corrosion. This is the role of cathodic protection. The method is shown schematically in **Figure 8.31**. There are two methods that are commonly used. One, shown in **Figure 8.31a**, consists of setting up a galvanic cell where the anode is any metal with a contact potential that is more negative than the contact potential of the protected metal. This forces electrons to flow from the anode to the cathode (iron) in opposition to the oxidation process above. In the process, the anode is consumed (it is sacrificial) and eventually must be replaced. In the cathodic protection of iron, the most common anode is zinc. It has a contact potential of -1.1 V , whereas the contact potential of iron can vary between -0.2 and -0.8 V , depending on the composition and treatment (e.g., steel is less active and hence has a less negative contact potential than, say, cast iron). There are other materials that can be used, most notably magnesium alloys (contact potential of -1.5 to -1.7 V) and aluminum (contact potential of -0.8 V). The second method is an active method shown in **Figure 8.31b**. It consists of a nonsacrificial anode and a power supply that produces the countercurrent. The anode may be an iron alloy, but can be graphite or, in some cases, a platinum-coated wire. The current is adjusted to counter the oxidation electron flow, usually by measuring the contact potential and ensuring it is below -1.0 to -1.1 V .

8.10 | PROBLEMS

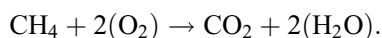
Units

8.1 Composition of air. The approximate composition of dry air by volume at 20°C is as follows: nitrogen (N_2) 78.09%, oxygen (O_2) 20.95%, argon (Ar) 0.93%, and CO_2 0.03%.

- Calculate its composition by mass. Assume air is an ideal gas at an ambient pressure of 1 atm (101,325 Pa) and temperature of 20°C.
- Calculate the composition of air in mol/m³. The air density at 20°C and an ambient pressure of 1 atm is 1.2 kg/m³.
- Calculate the number of atoms (molecules in the case of CO₂) per cubic meter (m³) of air for each constituent.

Note: There are many other constituents in air, but the four included here are the most important in terms of quantities.

- 8.2 Burning of natural gas.** The reaction that takes place during the burning of natural gas (methane [CH₄]) is as follows:

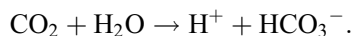


In the process, the reaction produces heat at a rate of 890 kJ/mol. Air is at an ambient pressure of 1 atm and a temperature of 20°C. Under these conditions, air contains 21% oxygen by volume or 23% oxygen by mass.

- Calculate the necessary proportions of gas and air by volume to produce complete burning of the gas.
- Calculate the necessary proportions of gas and air by mass to produce complete burning of the gas.
- Natural gas is delivered to a furnace at a pressure of 2 atm at 20°C. Calculate the heat generated per cubic meter of natural gas.

- 8.3 Molar mass and gram-equivalent.**

- Calculate the molar mass of CO₂.
- Calculate the molar mass of magnesium.
- Calculate the gram-equivalent of CO₂ dissolved in water. The solution of CO₂ in water is as follows:



- Calculate the gram-equivalent of magnesium ions in water (Mg⁺⁺).

- 8.4 Conversion between units.** A total of 0.01 mol of sulfuric acid (H₂SO₄) is mixed into 1 L of distilled water (H₂O). The density of water is 1 g/cm³ and that of sulfuric acid is 1.84 g/cm³. Calculate the concentration of sulfuric acid in ppm as

- A mass fraction.
- A volume fraction.

Metal oxide sensors

- 8.5 Oxygen sensor in internal combustion engines.** The use of oxygen sensors to reduce emission of noxious gases in internal combustion engines is mandated by the need to comply with pollution regulations. The sensor is used to sense the ratio

between the oxygen concentration in air and in the combustion stream and control the intake of oxygen to reduce emissions. The concentration of oxygen in air is approximately 20.9% (by volume). Calculate the range of readings of the oxygen sensor in the exhaust stream from conditions of no combustion (20.9% oxygen in the exhaust stream) to 4% oxygen in the stream. The exhaust is at a temperature of 600°C.

Note: It is desirable that a certain percentage of oxygen remains in the stream to allow the catalytic converter to operate and remove some of the combustion by-products such as CO. However, too much oxygen leads to lean combustion and can cause overheating of the engine.

8.6 Carbon monoxide sensor. The CO sensor in **Figure 8.1** is used to detect CO in a home and provide an alarm for concentrations greater than 50 ppm (the maximum allowable long-time workplace exposure level in the United States). To calibrate the sensor, its resistance is measured at 10 ppm and 100 ppm CO. The measured values are 22 k Ω and 17 k Ω , respectively. Calculate the sensor reading at which the alarm is triggered and the sensitivity of the sensor.

8.7 Metal oxide sensors and temperature variations. The resistance of metal oxide sensors depends on, among other things, temperature since the conductivity of the metal oxide is temperature dependent. The change in resistance as a measure of the concentration of the analyte relies on the fact that the temperature of the sensor is constant. Consider a thin film tin oxide sensor operating at 300°C used to sense CO. The calibration values are 16.5 Ω at a concentration of 75 ppm and 492 Ω at a concentration of 15 ppm. The conductivity of tin oxide is 6.4 S/m at 20°C and its temperature coefficient of resistance is $-0.002055/^{\circ}\text{C}$.

Note: Tin oxide, unlike many other metal oxide materials, has relatively high electric conductivity.

- Calculate the sensitivity of the sensor throughout its range and at the two given calibration points.
- Calculate the relative error in the base conductivity of the material due to variations of temperature around the base temperature of 300°C.
- Discuss the implications of the result in (b).

8.8 Sensing of oxygen in molten steel. An oxygen sensor similar to that shown in **Figure 8.5** is used to sense the oxygen concentration during the production of steel. The temperature of molten steel is kept a little above the melting point at 1550°C to ensure its flowing properties. The concentration of oxygen in air at that temperature is 18.5%. Oxygen is required in steel processing to react with carbon and hence produce low carbon steel. At the end of the process, excess oxygen must be removed, with residual oxygen in steel typically at about 100 ppm (by volume).

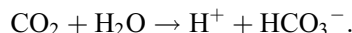
- Calculate the emf expected from the sensor at a concentration of 100 ppm oxygen assuming the output is zeroed for equal concentrations for oxygen in air and steel.
- Calculate the sensitivity of the sensor for oxygen concentrations in steel.

Solid electrolyte sensor

- 8.9 Pollution control in a wood-burning stove.** Wood-burning stoves and hearths are a pleasant source of heat on a cold winter day, but they are highly polluting, and unless properly ventilated they can be dangerous. In an attempt to control pollution an oxygen sensor is placed in the flue and used to control a fan that supplies the necessary additional air to properly burn the wood and reduce pollution. The temperature of the flue is 470°C and the oxygen level in the flue should not go below 8%. The normal oxygen level in the interior of a house is 20%. The system is set to keep the oxygen level between 8% and 12%. To ensure that the temperature of the flue does not rise too much, the fan is turned on when the oxygen level decreases to 8% and is turned off when it reaches 12%. Calculate the sensor output voltages at which the fan turns on and off.

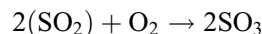
Glass membrane sensors

- 8.10 pH measurements.** In a pH meter the reading of the device is calibrated in pH values from 1 to 14. The actual meter is a high-impedance voltmeter and measurements are done at an ambient temperature of 24°C .
- Calculate the range of voltages the voltmeter must be capable of displaying for the range of pH between 1 and 14 given a Ag/AgCl reference electrode.
 - Calculate the range of errors per $^{\circ}\text{C}$ for the range of pH between 1 and 14.
- 8.11 Effect of CO_2 absorption on the pH of water.** Water absorbs CO_2 with a maximum concentration of 1.45 g/L. If neutral water ($\text{pH} = 7$) is left for long periods of time exposed to air it will absorb CO_2 from the air and become increasingly acidic, although the absorption rate is slow. The reaction responsible for the increase in acidity of water is the following:



Calculate the pH of initially neutral water after it has absorbed 1.45 g of CO_2 per liter.

- 8.12 pH and acid rain.** Although rainwater is in itself slightly acidic (with a pH between 5 and 6), whenever the pH is below 5 the rain is considered to be acidic, and hence detrimental to the environment. The causes of acid rain are mostly emissions from power plants, vehicles, and other chemical pollutants. CO_2 is one source (see **Problem 8.11**), but the source of most concern is sulfur dioxide (SO_2), whose main source is the burning of coal, primarily in coal-fired power plants, but also from vehicles and from volcanic eruptions. The reaction that occurs in the atmosphere is the following:



followed by



Sulfuric acid in water produces hydrogen cations and SO_4 anions:



To understand the problem of acid rain, consider an atmospheric concentration of 2 ppm SO_2 . Assuming that 0.5 ppm SO_2 is absorbed by falling rain that in the absence of SO_2 in the atmosphere would have a pH of 5.3, what is the pH of the rainwater after absorption of SO_2 ?

Soluble inorganic salt membrane sensors

- 8.13 Chloride ion sensor.** A silver chloride mixed with silver sulfide ($\text{Ag}_2\text{S}/\text{AgCl}$) membrane is used to sense low concentrations of chloride in water by detecting the Cl^- ion. With a Ag/AgCl reference electrode, the instrument measures a potential of 0.275 V at 32°C . Calculate the concentration of chloride in the water.
- 8.14 Lead sensor and errors.** To sense lead in water, one can use a Ag_2S membrane mixed with lead sulfide (PbS). The membrane senses the Pb^{2+} ion. Suppose a concentration of 100 ppm is measured, calibrated at 25°C using a saturated calomel reference electrode in a normal pH meter (intended to sense hydrogen in water).
- Calculate the potential expected across the electrodes.
 - What is the error in reading of the concentration if the temperature rises to 30°C and if no compensation for temperature is provided?

Thermistor-based chemical sensors

- 8.15 Blood glucose sensor.** To sense the concentration of glucose in blood for the purpose of monitoring diabetes, one can use a thermistor coated with the enzyme glucose oxidase and sense the temperature of the thermistor. Normal glucose levels in blood are between 3.6 and 5.8 mmol/L. Glucose has the formula $\text{C}_6\text{H}_{12}\text{O}_6$ and has an enthalpy of 1270 kJ/mol. The thermistor has a heat capacity of 24 mJ/K (the heat capacity for thermistors is typically given in mJ/K, a quantity that takes into account its mass) and a nominal resistance of 24 k Ω at 20°C . Assume the enzyme samples 0.1 mg of blood. Assume as well that blood is mostly water. The sensing is done at the normal blood temperature of 36.8°C .
- Calculate the increase in temperature of the thermistor over the range of normal glucose levels in blood.
 - Calculate the sensitivity of the sensor over the span given.
 - If, in addition, one measures the resistance of the thermistor as 18.68 k Ω at 30°C , calculate the range and span of the resistance of the thermistor and its sensitivity in terms of the resistance measured.
- 8.16 Sugar (sucrose) sensor for sugar production.** In the production of sugar from sugar cane, the stalks are first chopped and pressed to yield a juice from which sugar is refined. Sugar cane produces a juice with a typical sugar concentration in water of 13% by mass. To sense the concentration the sucrose phosphate

synthase enzyme can be used in a thermistor-based sensor to catalyze the sugar. Sucrose has the formula $C_{12}H_{22}O_{11}$ and an enthalpy of 5644 kJ/mol. A 12 k Ω thermistor (at the solution temperature) with a heat capacity of 240 mJ/K and a self-heat of 0.05 $^{\circ}\text{C}/\text{mW}$ is employed for this purpose.

- If the sensor samples 0.2 mg of the solution, calculate the sensitivity of the sensor in $^{\circ}\text{C}$ per percent sugar.
- If a current of 1.8 mA through the thermistor is required to operate the sensing circuitry, what is the error expected due to self-heat, neglecting the change in resistance of the sensor due to the change in temperature of the sensor when sugar is sampled?

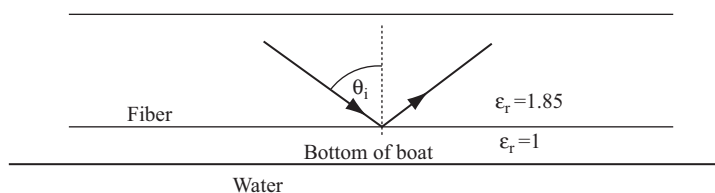
Catalytic sensors

- 8.17 Methane detector in mines.** A catalytic sensor based on a pellistor can be used to detect the methane concentration in mines to alert miners when the concentration is too high. The sensor is calibrated in LEL showing the percentage of LEL. Methane has the formula CH_4 and an enthalpy of 882 kJ/mol. The pellistor is based on alumina with a heat capacity of 775 J/kg/K, a mass of 0.8 g, and the platinum heater has a resistance of 1250 Ω at the operating temperature of 540 $^{\circ}\text{C}$. If the sensor samples a volume of 0.75 cm^3 of air, calculate the sensitivity of the sensor in ohms per percent LEL. The air and methane before sampling are at a temperature of 30 $^{\circ}\text{C}$ and the ambient pressure is 101,325 Pa (1 atm).

Optical chemical sensors

- 8.18 Water leakage sensor.** An evanescent loss sensor uses an optical fiber to sense water leakage into the bottom of a boat. The fiber is strung close to the interior surface of the boat, but not touching it, so it does not detect condensation of water at the bottom. To ensure that the sensor will only detect water, the angle of incidence of the laser beam (see **Figure 8.32**) is adjusted so that the total reflection occurs at all permittivities lower than that of water. The relative permittivity of glass at optical frequencies is 1.65 and that of water is 1.34. Detection occurs when the power transmitted along the optical fiber decreases because of transmission into the water through the interface.
- Calculate the angle of incidence, θ_i , of the light beam to ensure that water will be detected.

FIGURE 8.32 ■
Water leakage sensor.



- b. If one wishes to detect any medium with relative permittivity $\epsilon_r \leq 1.65$ in contact with the fiber rather than limiting this to water, what is the incidence angle θ_i ?

8.19 Petroleum leakage sensor. The sensor in **Figure 8.20** is used to detect petroleum leakage or water leakage from petroleum-transport hoses. These hoses are made with a double wall, as shown in **Figure 8.33**, with the sensor between the two walls. The purpose of the sensor is to detect oil leaking out through the inner hose or water leaking in through the outer hose. One simple method of detecting both oil and water is to use two sensors, one set to detect oil, the other set to detect water (a single sensor can be used as well with appropriate detection electronics). The relative permittivity of seawater at optical frequencies is 1.333, the relative permittivity of oil is 1.458, and the relative permittivity of the polycarbonate fiber used for the sensor is 1.585 (at the infrared frequency used for detection).

- Calculate the range of angles of incidence required in sensor 1 so it will detect water.
- Calculate the angle of incidence required in sensor 2 so it will detect oil.
- Will sensor 1 detect oil as well?
- Will sensor 2 detect water as well?
- If the answer to (c) or (d) is yes, show what the two sensors will show under various conditions (no leakage, oil leakage, or water leakage) and how detection of water and oil can be guaranteed to be positive.

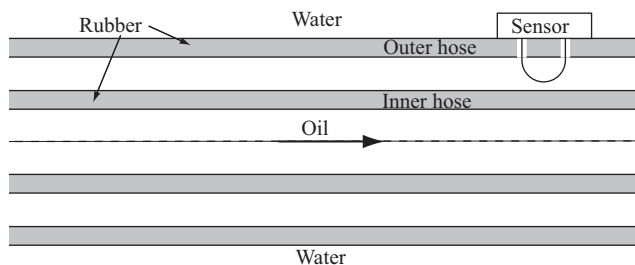


FIGURE 8.33 ■

A leakage sensor in the space between two rubber walls.

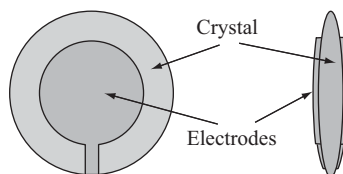
Mass sensors

8.20 Measurement of corrosion rate using a crystal microbalance. The crystal microbalance is an important analytical tool capable of high sensitivities and is commonly used in the laboratory. In one of its common forms a crystal disk is coated with opposite electrodes, typically of gold, and designed to resonate at a given frequency, typically between 6 and 18 MHz. The disk is connected to an oscillator and oscillates at its fundamental frequency. Any change in the mass of the disk changes the frequency. To measure the corrosion rate of iron in moist air, a crystal microbalance is used after one or both electrodes is coated with iron. In **Figure 8.34** the gold electrodes are 8 mm in diameter and the crystal disk is designed to oscillate at 10 MHz. A coating of 0.5 mg of iron is deposited on each

of the gold disks, covering them entirely. The crystal used has a sensitivity factor of $54 \text{ Hz} \cdot \text{cm}^2 / \mu\text{g}$.

- Calculate the resonant frequency before corrosion occurs.
- The rate of corrosion is measured in mm/year, that is, the thickness of material in millimeters corroded in 1 year. Assuming the instrument can reliably detect a change in frequency of 10 kHz, calculate the sensitivity of the microbalance in this application. The density of iron is 7.87 g/cm^3 .

FIGURE 8.34 ■
A gold-plated crystal
used for mass
sensing.



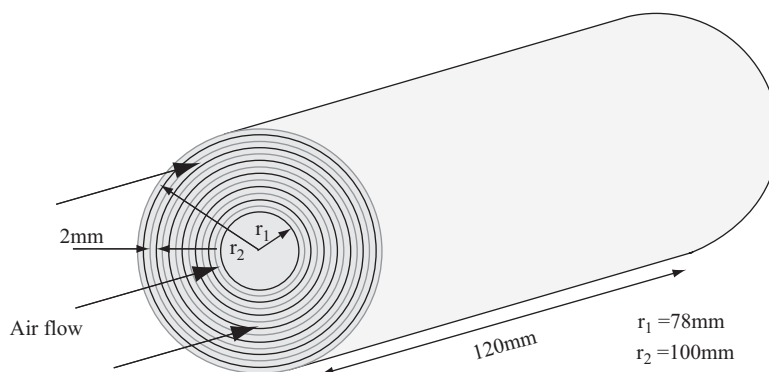
Humidity and moisture sensors

8.21 Capacitive humidity sensor. A simple humidity sensor, although not the most sensitive, may be obtained by measuring the capacitance of an air-filled parallel plate capacitor. Consider a capacitor with two plates, each 4 cm^2 in area with a 0.2 mm separation between plates.

- Calculate and plot the capacitance expected from the sensor for the range between 10% RH and 90% RH at an ambient temperature of 25°C .
- Calculate the sensitivity of the sensor.

8.22 Clothes drying humidity sensor. To control the drying process in a clothes drier a humidity sensor is an integral part of the process. There are many types of sensors that can be used. Consider the possibility of a capacitive sensor built in line with the air exhaust of the drier. The sensor (see **Figure 8.35**) is made of a series of concentric tubes, 12 cm long. There are a total of 14 tubes, with the outer tube equal in diameter to the exhaust tube (100 mm) and separated 2 mm apart to allow air to flow between the tubes. The inner tube is 76 mm in diameter. Alternating tubes are connected together (i.e., lighter shaded tubes are all

FIGURE 8.35 ■
A capacitive
humidity sensor.



connected together and darker shaded tubes are connected together to form a multiconductor coaxial capacitor). Approximate the capacitance of the cylindrical capacitor by the parallel plate equivalent, where the area of the plates is the average between the area of the outer and inner plates.

- Calculate the sensitivity of the sensor in pF/%RH.
- If the temperature in the exhaust varies during the drying process from 50°C to 75°C, what is the variation in sensitivity expected?

8.23 Relative humidity sensing. The dew point temperature is measured using the device in **Figure 8.28** at an ambient temperature of 32°C and was found to be 22.6°C. Calculate the relative humidity in air.

8.24 Dew point versus relative humidity. Calculate and plot the dew point temperature at 27°C as the relative humidity varies from 0% to 100%. Use increments of 10°C.

8.25 Capacitive humidity sensor. The following data were collected for a capacitive humidity sensor based on an alumina hygroscopic layer at 20°C and at 60°C. The capacitance of the sensor at 0% humidity is 303 pF and the relative permittivity of (dry) alumina is 9.8. Assume a parallel plate capacitor structure.

Relative humidity [%]	0	10	20	40	60	80	90
Capacitance at 20°C [pF]	303	352	432	608	858	1216	1617
Capacitance at 60°C [pF]	303	345	394	508	655	845	963

- Calculate the amount of water absorbed by the alumina layer at 20°C if its volume is 0.8 mm³. Plot the amount of water (mass) absorbed as a function of relative humidity. The density of water is 1 g/cm³ and the relative permittivity is 80.
- At 60°C the relative permittivity of water reduces to 72. Calculate the amount of water (mass) absorbed and compare it with that at 20°C. Plot both.
- Discuss the consequences of the results in (a) and (b) on the performance of the sensor. In particular, address the issues of response time (including the time needed to remove the moisture) and sensitivity to temperature variations.

8.26 Dew point humidity sensor. The dew point humidity sensor is one of the most accurate methods of sensing relative humidity, even though it is not the most convenient. In applications where accuracy is important this inconvenience is a minor issue. In a measurement the dew point sensor temperature is found to be 37°C at an ambient temperature of 90°C. Calculate the relative humidity of air.

8.27 Dew point humidity sensor. Show that the dew point temperature cannot be higher than the ambient temperature in two ways:

- Theoretically.
- By using a dew point temperature of 30°C at an ambient temperature of 25°C.

8.28 Sensitivity and resolution of the dew point sensor.

- Calculate the sensitivity of the dew point sensor as a relative humidity sensor.
- If the temperature sensor in **Figure 8.28** is capable of a resolution of ΔT_d [°C] at an ambient temperature T_a for which the dew point temperature is T_d , what is the resolution of a humidity sensor based on the dew point sensor?

8.29 Relative humidity as a function of dew point temperature. Calculate and plot the relative humidity at ambient temperatures $T = 20^\circ\text{C}$, 25°C , and 30°C as the dew point temperature varies from -20°C to T . Use increments of 1°C .**Chemical actuation****8.30 Pollution and power loss in diesel engines.** A small diesel engine is used to generate power. The generator output is 10 kW. The engine has a rated efficiency of 50% and consumes a common diesel fuel with rated energy of 32 MJ/L. The four-cylinder, four-stroke engine runs at a constant 1200 rpm and has a displacement of 850 cc. A catalytic converter is used to reduce CO emissions from 7000 ppm to 25 ppm as required by law. The density of air is 1.2 kg/m^3 (at 20°C) and the properties of CO are a specific heat capacity of 29 J/mol/K and an enthalpy of combustion in oxygen of 283 kJ/mol.

- Calculate the power generated by the conversion of CO in the catalytic converter (power is energy per unit time [J/s]). Assume air intake is at the ambient temperature (20°C).
- Calculate the efficiency of power generation and estimate the reduction in fuel consumption (in percent) if the engine emitted no CO at all, assuming the energy that otherwise would be generated in the converter is recovered in the engine itself. In estimating the reduction in fuel consumption, assume that fuel consumption is linearly related to power output, that is, if the output power is reduced by $x\%$, fuel consumption is reduced by the same percentage.

Note: We usually think of pollution in terms of its negative effects on us and the environment, and of pollution control as a necessary, sometimes costly process. However, pollution has other costs, as this example shows, and elimination of pollution through the use of clean fuels and complete combustion has significant benefits.

8.31 Design of an airbag. A 75 L airbag must inflate to a peak pressure of 180 kPa. The nominal temperature for the design is 20°C .

- Calculate the amount (mass) of NaNH_3 propellant needed to achieve that. Neglect the increase in temperature of the gas during the reaction and assume inflation is entirely due to nitrogen gas generated during the reaction.
- Given the amount (mass) of propellant calculated in (a) with the bag deploying at 0°C and no increase in the temperature of the gas during the reaction, what is the pressure expected in the bag?

- c. The reaction that generates nitrogen gas does increase the temperature of the gas. Suppose the temperature rises by 50°C above ambient. What are the answers to (a) and (b) now?

Note: Pressure regulation in airbags is rudimentary but is an essential part of safety. Too high a pressure and injury might occur due to impact with the bag, whereas too low a pressure defeats the purpose of the airbag and can result in injury. For this reason, most airbags have some means of controlling pressure.

8.32 Compressed nitrogen airbag system. In principle, one can use compressed nitrogen to inflate airbags, avoiding the need for explosives and unstable materials. However, this is not as simple as it sounds, primarily because of the volume and pressure needed. Suppose a container capable of withstanding a pressure of 2.5 MPa is used to inflate a 105 L airbag (a typical airbag volume) to a pressure of 175,000 Pa.

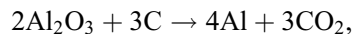
- What must be the volume of the container, assuming an ambient temperature of 30°C and that there is no increase in temperature during inflation and the gas container is also at 30°C .
- Expanding gas cools during expansion. If one can assume a decrease in gas temperature of 30°C during inflation, what is the necessary volume of the container, assuming the same pressure? The ambient temperature is 30°C .
- Because vehicles are designed to operate and be stored at elevated temperatures, the container designed in (a) or (b) must withstand the additional pressure due to changes in temperature. Assuming the container must be able to withstand temperatures between -60°C and $+75^{\circ}\text{C}$ (to allow for a reasonable margin of safety), what is the minimum and maximum pressure expected in the container?
- What are your conclusions from the results above?

8.33 Resistive electroplating coupon. In an attempt to control plating thickness one can use a resistive coupon—a simple wire or strip made of the base material on which electroplating is performed. The resistance of the coupon changes with the coating thickness, and by measuring this resistance one can stop the coating process at the right time. Suppose electroplating of nickel on iron is performed and the nickel thickness required is $10\text{ }\mu\text{m}$. A coupon is made as a very thin strip 4 cm long, 1 cm wide, and 0.5 mm thick of the same iron grade.

- Calculate the change in resistance of the coupon from no plating to $10\text{ }\mu\text{m}$ nickel plating. The conductivities of iron and nickel are $1.12 \times 10^7\text{ S/m}$ and $1.46 \times 10^7\text{ S/m}$, respectively.
- The density of nickel is 8900 kg/m^3 . If the coating thickness is achieved in 8 min, 35 s, what is the current density used in the plating process?

Note: The measurement of resistance must be made out of the solution, otherwise the resistance is affected by the solution itself, which is conductive. The coupon can be reused, but the calibration (zero coating resistance) changes and must be measured before electroplating begins.

8.34 Aluminum production. Aluminum is produced in an electrolytic process essentially identical to the electroplating process except that the electrodes used are carbon (graphite) and the process is done at high temperatures so that aluminum is in its liquid state. The process starts with alumina (Al_2O_3) in molten cryolite (Na_3AlF_6). The latter serves to conduct electricity. The process is called the Hall process and is as follows:



with carbon coming from the graphite electrodes and CO_2 being emitted as gas. To operate, a typical voltage of 4.5 V is used to generate a current of 100 kA.

- Calculate the time it takes to produce one ton of aluminum.
- Calculate the energy needed per ton of aluminum.
- Calculate the mass of CO_2 released per ton of aluminum.
- Calculate the mass of carbon needed for the process per ton of aluminum.